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## Heterogeneous Acidic TiO<sub>2</sub> Nanoparticles for Efficient Conversion of Biomass Derived Carbohydrates<sup>†</sup>

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Selective conversion of biomass derived carbohydrates into fine chemicals is of great significance for the replacement of petroleum feedstocks and the reduction of environmental impacts. Levulinic acid, 5-hydroxymethyl furfural (HMF) and their derivatives are recognized as important precursor candidates in a variety of different areas. In this study, the synthesis, characterization, and catalytic activity of acidic TiO<sub>2</sub> nanoparticles in the conversion of biomass derived carbohydrates were explored. This catalyst was found to be highly effective for selective conversion to value-added products. The nanoparticles exhibited superior activity and selectivity towards methyl levulinate from fructose in comparison to current commercial catalysts. The conversion of fructose to methyl levulinate was achieved with 80 % yield and 15 high selectivity (up to 80 %). Additionally, conversions of disaccharides and polysaccharides were studied. Further, the production of versatile valuable products such as levulinic esters, HMF, and HMF-derived ethers was demonstrated using the TiO<sub>2</sub> nano-sized catalysts in different solvent systems.

#### 1. Introduction

Since the use of fossil fuels as feedstocks for fine chemical <sup>20</sup> synthesis and energy resources is approaching unsustainable levels, the development of innovative strategies and resources for the sustainable production of fuels and chemicals from renewable materials are stimulating interest.<sup>1-4</sup> Among these resources, biomass has attracted enormous attention due to its considerable <sup>25</sup> potential as a raw material for the production of green fine chemicals, fuels and fuel additives.<sup>5</sup> Therefore, it is highly desirable to convert carbohydrates to platform molecules selectively under mild conditions, which can subsequently be used for the production of various chemicals. The typical <sup>30</sup> approach for biomass degradation involves acid-catalyzed hydrolysis<sup>6</sup> followed by either chemical or biological conversion to monosaccharides.<sup>7</sup> For example, glucose produced from cellulose through hydrolysis in an aqueous medium can be

transformed to useful molecules such as alkyl glucosides, 5-<sup>35</sup> hydroxymethyl furfural (HMF),<sup>8</sup> levulinic acid, and gluconic acid.<sup>9</sup> Among these valuable molecules, levulinic acid and ester derivatives are among the most promising building blocks in a biomass refinery. Levulinic acid and its esters are classified as some of the top 12 valuable chemicals converted from biomass

<sup>40</sup> according to the US Department of Energy's National Renewable Energy Laboratory (NREL).<sup>10</sup> Levulinic acid can also be converted into other useful chemicals such as acrylic acid, succinic acid, pyrrolidines, and diphenolic acid.<sup>11, 12</sup>

A traditional approach to the synthesis of levulinic acid from <sup>45</sup> biomass-derived carbohydrates requires the use of homogeneous mineral acids such as sulfuric acid and metal chloride salts.<sup>13-16</sup> The use of homogeneous catalysts for biomass conversion has been extensively studied and is known to be highly effective. However, there are several drawbacks to this approach, including extension end according to the several drawbacks to the seve

<sup>50</sup> catalyst separation, reactor corrosion, and recyclability. Recently, there have been several studies conducted regarding direct

synthesis of platform molecules from biomass-derived feedstocks such as cellulose<sup>17</sup>, saccharides<sup>18</sup>, and furfuryl alcohol<sup>19</sup> using various acids and solvents. Essayem et al. proposed a method for <sup>55</sup> the direct synthesis of methyl levulinate from cellulose using solid acids in supercritical MeOH.<sup>17c</sup> Wang and co-workers developed an acid and metal free method for converting fructose to HMF using an ionic liquid system.<sup>18d</sup> Mascal et al. investigated the process of producing HMF derived ethers and levulinic acid <sup>60</sup> by 5-(chloromethyl)furfural (CMF).<sup>19d</sup> Furthermore, Tominaga et al. explored the Lewis and Brønsted mixed-acid systems as an efficient way to synthesize methyl levulinate.<sup>17d</sup> Despite all of the afore-mentioned progress, development of novel heterogeneous, cost-effective and efficient catalysts for direct synthesis of <sup>65</sup> platform molecules from biomass resources is imperative for the production of useful chemicals from biomass resources.

The proposed synthetic pathways<sup>20</sup> for the direct conversion of monosaccharides using acid catalysts are shown in Scheme 1. The reaction starts with the isomerization of glucose to fructose 70 followed by the Brønsted-acid-catalyzed dehydration to produce HMF. Subsequent rehydration of HMF yields levulinic acid. Further reaction of these acids (levulinic or formic acids) with alcohols can produce acid esters. HMF also reacts with alcohols to form HMF derived ethers under specific conditions. The 75 control of the acid type on the catalyst surface is crucial for its selectivity, since different acid types determine the formation of different products. Several solid acids have been widely utilized to convert carbohydrates, such as zeolites,<sup>21</sup> metal oxides,<sup>22</sup> polymer based acids,<sup>20</sup> and heteropoly acids.<sup>23</sup> Although solid 80 acids are more easily separated, recycled, and environmentally benign, there are still considerable opportunities for improving the selectivity and mass transfer limitations between the insoluble polymers and heterogeneous catalysts.

Herein, we report the facile synthesis of acidic TiO<sub>2</sub> <sup>85</sup> nanoparticles that can be used as catalysts in biomass derived carbohydrate conversion. In addition, several other solid acids such as zeolites, polymer based acids, and sulfated metal oxides were chosen for comparison. Detailed process parameters including reaction time, temperature, catalyst loading, and the reusability of the catalyst were investigated in terms of catalytic performance. Moreover, different carbohydrate sources and s solvents were studied.

**Scheme 1.** Proposed reaction pathway for the conversion of carbohydrates to platform molecules

#### **10 2. Experimental Section**

#### 2.1 Catalyst preparation

All chemicals were purchased from Sigma-Aldrich and used without further purification. P-25 were purchased from Degussa <sup>15</sup> Inc.. H-ZSM5 (Si/Al = 50) and H-Beta (Si/Al = 30) were

- purchased from Zeolyst Inc. and calcined at 550 °C before use. Sulfated  $ZrO_2$  and  $TiO_2$  were made from the corresponding hydroxides prepared by hydrolysis of a 0.4 M aqueous solution of the metal precursor with NH<sub>4</sub>OH (25 wt% in water) at r.t. under
- <sup>20</sup> vigorous stirring, at a given final pH of  $\sim 10$ . The hydroxides were then impregnated (via an incipient wetness technique) with 0.5 M sulfuric acid and dried at 150 °C.<sup>24</sup> Finally, all the samples were calcined in the air at temperatures between 450  $\sim 650$  °C with a soak time of 3 h.
- <sup>25</sup> The TiO<sub>2</sub> nanoparticles were synthesized via modified precipitation of TiOSO<sub>4</sub>.xH<sub>2</sub>SO<sub>4</sub> (Alfa Aesar) with ammonia solution at 85 °C. The pH value of the solution was controlled under acidic conditions during precipitation. The resulting

suspension was then refluxed overnight. Impurities and by-<sup>30</sup> products, such as excessive SO<sub>4</sub><sup>2-</sup> and NH<sup>4+</sup> ions, were removed by filtration and washing with an adequate amount of distilled deionized water until the filtrate pH was neutral. The obtained white powder was then dried overnight at 120 °C.

#### 35 2.2 Catalyst characterization

The catalyst was characterized by powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA), temperature programmed <sup>40</sup> desorption (TPD), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption/desorption [Brunauer-Emmett-Teller (BET) surface area]. The acid types of the catalysts were determined by pyridine-adsorption and FT-IR experiments. The amount of acid sites was determined by thermogravimetric titration using 2,6 <sup>45</sup> lutidine and 3,5 lutidine.<sup>25</sup> The detailed methods are presented in the ESI.

#### 2.3 Typical condition for biomass conversion reaction

Carbohydrate conversion experiments were carried out in a 100 mL cylindrical stainless steel pressurized reactor made by PARR <sup>50</sup> Instrument Company, USA. In a typical reaction, 1 mmol of monosaccharide (0.18 g of fructose/glucose), 0.5 mmol of disaccharide (0.18 g of sucrose/ cellobiose) or biomass sources (molecular weight of cellulose and starch are calculated as a glucose unit) were used as substrates. Catalyst (0.01 to 0.20 g) <sup>55</sup> and solvent (20 mL) were charged into the reactor, followed by purging with nitrogen, and pressurizing to 20 bar. The reactor was then heated to designated temperatures for different reaction times with stirring. After the reaction mixture was centrifuged <sup>60</sup> and filtered to remove the catalyst and insoluble solids before

- and intered to remove the catalyst and insoluble solids before analyses. For testing of the reusability of the catalyst, the catalyst was collected by centrifugation after reaction, then washed with methanol (20 mL) twice and dried at 100 °C before reuse. The catalyst was regenerated by calcining under air at 400 °C for 1 h.
- 65 The detailed conversion and yield calculations are presented in the ESI.

#### 3. Results and discussion

#### 70 3.1 Catalytic conversion of fructose to methyl levulinate

The catalytic performance of the TiO<sub>2</sub> nanoparticles was first tested by fructose conversion in MeOH (Fig. 1). The reaction started with dehydration of fructose to HMF followed by rehydration of HMF to levulinic acid. Finally, levulinic acid was <sup>75</sup> further converted to methyl levulinate (ML) by esterification with MeOH. In primary temperature-dependent studies using fructose as a substrate, TiO<sub>2</sub> nanoparticles exhibited moderate activity (93 % conversion and 4 % ML yield) when the reaction temperature was below 100 °C; however, when the temperature was increased <sup>80</sup> to 150 °C, the yield of ML was enhanced to 79 %. It was not until 225 °C that the yield of ML dropped to 68 %. This drop is probably due to decomposition of ML at higher temperatures. In



addition, HMF and levulinic acid were barely detected in any experiment throughout this study, indicating rapid rehydration of HMF and esterification to produce ML. Typically, the formation of humins either from sugar decomposition or HMF oxidation is

- <sup>5</sup> believed to be the main factor that lowers the ML yield.<sup>26</sup> Therefore, the origin of humins was further investigated by FT-IR analyses (see ESI† Fig. S1). For these analyses, formed humins were collected from two separate reactions utilizing fructose and HMF as substrates, respectively. Both FT-IR spectra showed <sup>10</sup> similar features, such as several broad absorbance peaks located in 900 ~ 1800 cm<sup>-1</sup> region as well as two distinct peaks located at
- 1596 and 1716 cm<sup>-1</sup>. The latter two can be assigned to humins formed from aldol addition/condensation polymerization of 2,5dioxo-6-hydroxyhexanal (DHH), which is a highly active <sup>15</sup> intermediate formed from HMF. In addition, humins collected from the HMF reaction exhibited two additional peaks at 758 and 795 cm<sup>-1</sup>, which can be attributed to polymerized HMF.<sup>26b</sup> Thus, fructose and HMF polymerization are not the main sources for the formation of humins. Instead, the intermediate HMF is most <sup>20</sup> likely rapidly converted to ML contributing to the higher yields of ML at short reaction times.

To investigate the effects of catalyst loading on activity, different amounts of catalyst were used (see ESI<sup>†</sup> Fig. S2). The studies showed that TiO<sub>2</sub> nanoparticles exhibit high activity even <sup>25</sup> with lower catalyst loading. For example, only 5.5 wt% catalyst loading (with respect to fructose) was required for a 67 % yield of ML with 95 % conversion. The product mixture in methanol solution was analyzed by NMR without further purification and was identified as ML with minimal impurities (see ESI<sup>†</sup> Fig. S3). <sup>30</sup> In contrast to homogeneous acid catalyzed reactions, the purification process in this system only requires filtration and solvent removal, which affords a straightforward and economical approach.



<sup>35</sup> Fig.1 Influence of the reaction temperature on fructose conversion and ML yield. (*Reaction conditions:* 20 mL 0.05 M fructose in MeOH, 0.1 g TiO<sub>2</sub> nanoparticles, 1 h.)

### 3.2 Comparison of different catalysts for the conversion of 40 fructose to ML

The catalytic performances of TiO2 nanoparticles were compared to other TiO<sub>2</sub> materials and solid acid catalysts such as Amberlyst-15, sulfated ZrO<sub>2</sub> and TiO<sub>2</sub>, niobic acid, and H-type zeolites. Due to the fact that dehydration of fructose is associated 45 with the acidity of the catalyst,<sup>27</sup> the acidities of the solid catalysts were characterized by thermogravimetric titration using 2,6 and 3,5 lutidines.<sup>26b</sup> The catalytic results, surface areas, and acidities are summarized in Table 1. For the acid-catalyzed dehydration of fructose, commercial TiO2 was inactive under the 50 same conditions. P-25 did not show any rehydration ability; only HMF (20 %) was detected after reaction. Among the other tested solid acids, Amberlyst-15 showed the highest activity and niobic acid only produced a small amount of HMF (5 %). Sulfated ZrO<sub>2</sub> and TiO<sub>2</sub> showed the formation of the desired product ML in 55 moderate yields (62 % and 41 %, respectively). The catalytic results are strongly correlated with surface acidity. Among the studied materials, TiO<sub>2</sub> nanoparticles exhibited the most acidic sites as well as the largest surface areas. This might be the reason why TiO<sub>2</sub> nanoparticles were highly active for fructose 60 conversion. Moreover, the notable high activity of prepared acidic TiO<sub>2</sub> nanoparticles is attributed to its nano-sized nature. Ultra-sonicated TiO<sub>2</sub> in MeOH is able to remain in suspension for more than one week. Such behaviour minimizes mass transfer limitations under reaction conditions.

 $_{65}$  Classic acid-rich H-type zeolites like HZSM-5 and H-beta were also tested under the same reaction conditions. Thermogravimetric titration results showed that the acidities of HZSM-5 and H-beta catalysts were higher than that of TiO<sub>2</sub> nanoparticles. However, HZSM-5 and H-beta exhibited lower

- <sup>70</sup> selectivities for fructose conversion than the  $\text{TiO}_2$  nanoparticles. Both zeolites converted fructose not only to ML and methyl lactate but also unidentified side products. This might be due to the mixture of acid types in zeolites. The H-type zeolites contain both Brønsted and Lewis acid sites on the surface.<sup>28</sup> As shown in
- 75 Scheme 1, Brønsted acids allow reactions to undergo dehydration then rehydration to produce ML; Lewis acids, on the other hand, catalyze a retro-aldol reaction to generate methyl lactate. Also, the relatively stronger acidities of H-type zeolites were not suitable for fructose conversion under optimized conditions for
- $_{80}$  TiO<sub>2</sub> nanoparticles. Consequently, the selectivity toward ML was significantly lowered to 27~15 % for H-type zeolites. The TiO<sub>2</sub> nanoparticle catalyst provide appropriate acidity to catalyze both the dehydration and further rehydration of fructose.

#### 85 3.3 Investigations on conversion of different biomass sources

Investigation of the conversion of different biomass sources demonstrated the practical applicability of the synthesized TiO<sub>2</sub> catalyst (Table 2). In glucose conversion, the reaction pathway involves isomerization of glucose to fructose. Fructose is then <sup>90</sup> converted to ML in MeOH. The time-dependent studies (see ESI<sup>†</sup> Fig. S4) showed the co-existence of glucose and fructose in the first 5 hours, indicating a slow glucose isomerization. The yield of ML stabilized at a maximum of 61% after 9 hours. The rate of glucose isomerization controls the selectivity to ML. The use of <sup>95</sup> disaccharides such as sucrose (a disaccharide of glucose and

fructose) and cellobiose (a disaccharide of glucose) requires initial hydrolysis of disaccharide into the monosaccharides. Sucrose and cellobiose were also selectively converted to ML with high yields (65 % and 58 %, respectively), indicating that s sequential reactions

Table 1. Summary of catalytic results and	characterization for	r different solid	acid catalysts <sup>a</sup>
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			Yield / Selectivity (%)			N of Acid sites by N of Acid sites by	
Catalyst	Conversion (%) <sup>b</sup>	HMF <sup>b</sup>	ML <sup>c</sup>	MLA <sup>c</sup>	$(m^2/g)$	2,6 Lutidine µmol/g <sup>e</sup>	3,5 Lutidine μmol/g <sup>e</sup>
TiO <sub>2</sub> nanoparticles	>99	0/(0)	79/(80)	_ <sup>d</sup>	238	303	218
Commercial TiO <sub>2</sub>	23	3/(13)	0/(0)	-	18 <sup>g</sup>	19	20
P-25 TiO <sub>2</sub>	87	20/(23)	0/(0)	-	56 <sup>g</sup>	48	42
Sulfated ZrO <sub>2</sub>	89	25/(28)	62/(70)	-	106	207	154
Sulfated TiO <sub>2</sub>	82	33/(40)	41/(50)	-	98	144	127
Amberlyst-15	>99	0/(0)	66/(60)	-	35	457 <sup>f</sup>	457 <sup>f</sup>
$Nb_2O_5$	76	5/(7)	0/(0)	-	20	5	125
H-ZSM5	98	0/(0)	2(/(27)	21/(21)	426 <sup>g</sup>	272	(7)
(Si/Al =50)		0/(0) 20/(2	20/(27)	21/(21)		212	0/4
H-Beta (Si/Al =30)	72	0/(0)	11/(15)	23/(32)	680 <sup>g</sup>	607	628

<sup>*a*</sup> *Reaction conditions*: MeOH (20 mL), fructose (1 mmol), catalyst (0.1 g), 175 °C, 1 h under N<sub>2</sub>. The average yields are reported. <sup>*b*</sup> Conversions and yields of HMF were obtained by HPLC analysis. <sup>*c*</sup> Yields and selectivities of methyl levulinate (ML) and methyl lactate (MLA) were obtained by GC-FID analysis. <sup>*d*</sup> Not observed product. <sup>*e*</sup> The number of acid amount measurements were done by thermogravimetric titration method. <sup>*f*</sup> Due to the thermal <sup>10</sup> instability of Amberlyst-15, the acidity data was acquired from literature. <sup>31</sup> <sup>*g*</sup> acquired from literature. <sup>31</sup>

(hydrolysis of disaccharides, isomerization of glucose to fructose and finally conversion to ML) were successfully catalyzed. The main differences between the conversions of sucrose and cellobiose are the reaction times; sucrose only requires 3 hours <sup>15</sup> while cellobiose requires 9 hours to complete the reaction. This difference may be due to the hydrolysis of sucrose to glucose and fructose units, which is feasible for conversion of ML. Besides these monosaccharides (fructose, glucose) and disaccharides (sucrose, cellobiose), polysaccharides (cellulose and starch) were <sup>20</sup> also tested under the same conditions as fructose conversion. Both cellulose and starch reached ML yields around 40% after 20 hours. Conversion of cellulose to ML involves depolymerization of cellulose to glucose and the subsequent transformation of glucose to ML; therefore, a longer reaction time was needed for <sup>25</sup> this reaction. The depolymerization of cellulose/starch to glucose

may be hindered in organic solvents by solubility constraints.

**Table 2.** Methyl levulinate yields from different biomass carbohydrates catalyzed by TiO<sub>2</sub> nanoparticles<sup>a</sup>

Substrata	Yield / Selectivity (%)			
Substrate	Conversion (%) <sup>b</sup>	$ML^{c}$		
Fructose	>99	80/(80)		
Glucose	>99	61/(61) <sup>e</sup>		
Sucrose	82, >99	$51/(62), 65/(65)^d$		
Cellobiose	68, >99	17/(25), 58/(58) <sup>e</sup>		
Cellulose	72	$42/(58)^{f}$		
Starch	67	$40/(60)^{f}$		

<sup>30</sup> <sup>a</sup> Reaction conditions: MeOH (20 mL), fructose (1 mmol), catalyst (0.1 g), 175 °C, 1 h under N<sub>2</sub>. All reactions were repeated three times. The average yields are reported. <sup>b</sup> Conversions were obtained by HPLC analysis. <sup>c</sup> Yields and selectivities of ML were obtained by GC-FID analysis. <sup>d</sup> Reaction time: 3 hours. <sup>e</sup> Reaction time: 9 hours. <sup>f</sup> Reaction <sup>35</sup> time: 20 hours.

#### 3.4 Investigations on conversion in different solvents

Utilization of TiO<sub>2</sub> nanoparticles for converting fructose in various solvents was investigated, and the results are given in <sup>40</sup> Table 3. Fructose was dehydrated to HMF, but no further

rehydrated products such as levulinic acid were detected in aprotic solvents. Among all tested aprotic solvents, tetrahydrofuran (THF) gave the highest HMF yield (54 %). Although fructose solubility is higher in solvents with relatively <sup>45</sup> high boiling points [such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMA)] the use of these solvents produced more humins during the reaction (as indicated by a deep brown color observed after the reaction). The formation of humins suppressed the HMF yield in these <sup>50</sup> solvents.

Regarding the utilization of levulinic esters as diesel blend components, lower molecular weight levulinic esters have shown some disadvantages. ML is miscible with water, which is difficult to manage. Another disadvantage is that ML might separate from 55 biodiesel at low temperatures. However, higher molecular weight levulinic esters have higher octane numbers, which are thermally more stable. Mixing diesel with higher boiling point levulinic esters can also reduce volatile organic compound (VOC) emissions, and is more environmentally friendly.<sup>29</sup> Therefore, *n*-60 ethanol, propanol, and butanol were used as solvents in order to produce levulinic esters with higher molecular weights. The results showed that fructose converted to different *n*-alkyl levulinates can reach 71~ 78% yield in three hours. Zhang et al. tried to produce alkyl levulinates in high yields.<sup>29b</sup> However, the 65 expensive furfuryl alcohol was needed as a precursor while our process uses economical raw precursors such as fructose to produce versatile levulinic esters using a TiO<sub>2</sub> nanoparticle catalyst.

The formation of levulinic esters from fructose is a consecutive <sup>70</sup> reaction which probably proceeds by either rehydration of HMFether to form levulinic ester or by rehydration of HMF to levulinic acid, followed by esterification to form levulinic ester. Interestingly, the use of higher steric hindrance alcohols such as 2-propanol, 2-butanol and *t*-butanol led to the HMF-derived <sup>75</sup> ethers as main products as opposed to levulinic esters. The reaction was not favorable for further rehydration to form levulinic esters, so the generation of other products such as levulinic acid or esters was suppressed. The yields of HMF- derived ethers were 63 ~ 68% in 2-propanol, 2-butanol and *t*butanol. HMF-derived ethers such as 5-ethoxymethylfurfural have already been tested, and exhibited comparable energy density relative to standard gasoline.<sup>30</sup> The advantage of forming <sup>5</sup> HMF-derived ethers is that they are much more stable and easier to work with than HMF. Therefore, by adjusting *n*-alkyl alcohols to higher sterically hindered alcohols, another selection of valuable platform chemicals (HMF-derived ethers) was obtained.

**Table 3.** Effect of solvents on fructose conversions and products yields to catalyzed by TiO<sub>2</sub> nanoparticles<sup>a</sup>

		Conversion		Yie		
Solvent	Time (h)	(%) <sup>b</sup>	HMF <sup>b</sup>	HMF ether <sup>c</sup>	Levulinic ester <sup>c</sup>	$\mathrm{LA}^{\mathrm{b}}$
THE	1	>99	42	_d	-	-
IHF	3	>99	54	-	-	-
CH <sub>3</sub> CN	3	66	19	-	-	-
DMF	3	>99	31	-	-	-
DMSO	3	>99	30	-	-	-
DMA	3	>99	35	-	-	-
E4011	1	97	n.d.	18	58	n.d.
EIOH	3	>99	n.d.	n.d.	71	n.d.
" DrOII	1	98	n.d.	14	66	n.d.
<i>и</i> -ноп	3	>99	n.d.	n.d.	78	n.d.
2 DrOU	1	96	< 1%	52	8	2
2-ИОП	3	>99	< 1%	68	13	4
	1	>99	n.d.	12	67	n.d.
<i>n</i> -BuOII	3	>99	n.d.	n.d.	75	n.d.
2 BuOH	1	96	< 1%	54	4	2
2-BuOII	3	>99	< 1%	67	10	6
t-BuOH	1	98	9	45	3	8
	3	>99	7	63	7	9

<sup>a</sup> Reaction conditions: solvent (20 mL), fructose (1 mmol), catalyst (0.1 g), 150 °C, under N<sub>2</sub>. <sup>b</sup> Conversion and yield of HMF and levulinic acid were obtained by HPLC analysis. <sup>C</sup> Yields of levulinic esters and HMF-derived ethers were obtained by GC-FID analysis. <sup>d</sup> Not observed <sup>15</sup> product.

#### 3.5 Investigations of the catalysts reusability

Reusability is also a key factor in heterogeneous catalysis. Results indicate that the yields of ML gradually decreased to 40 <sup>20</sup> % after the 5th use (Fig. 2). The color of the catalyst changed from white to deep brown, indicating an accumulation of humins on the surface of catalyst over time, possibly causing deactivation. Therefore, post treatment of the catalyst was performed by calcination at 400 °C for 1 h. The white color of the <sup>25</sup> catalyst was restored, and the yields reverted to 70 % with only

- around a 10 % loss of yield after the 6th use. The recovered catalysts were further characterized. The XRD patterns (see ESI<sup>†</sup> Fig. S5) and SEM images (see ESI<sup>†</sup> Fig. S7) of recovered  $TiO_2$  nanoparticles showed no significant changes after calcination.
- $_{30}$  These characterization studies showed that the morphology of TiO<sub>2</sub> nanoparticles remained the same after reaction and regeneration.

Sulfated metal oxides are well known strong solid acid catalysts and are widely tested for catalytic reactions.<sup>31</sup> The main <sup>35</sup> drawback of sulfated metal oxides is the unstable activity due to sulfate leaching problems. Therefore, we compared the stability of TiO<sub>2</sub> nanoparticles to other sulfated ZrO<sub>2</sub> and TiO<sub>2</sub> prepared by impregnation methods. To reduce interferences, humins adsorbed on the catalysts were removed by calcination after each 40 use. The results are shown in Figure 2. The yield of ML from 80 % dropped to 70 % after the 3rd use but stabilized at around 70 % in further uses for TiO<sub>2</sub> nanoparticles. On the other hand, the activity of sulfated ZrO<sub>2</sub> and TiO<sub>2</sub> catalysts drastically dropped; both of the sulfated catalysts were almost completely deactivated 45 after the 5th use. Strong acidity for the sulfated catalysts is primarily due to the chelation of sulfate ions on the surface of metal oxides.<sup>31</sup> Therefore, the thermal stability of TiO<sub>2</sub> nanoparticles was also tested. In Table S2 (see ESI<sup>+</sup> Table S2), the results indicated the sulfur concentration of the TiO<sub>2</sub> 50 nanoparticles for different treatments. Almost no sulfur was detected for the catalyst calcined at 800 °C which showed no activity toward ML production. The deactivation might occur due to sulfate ion decomposition. Deactivation of the sulfated metal oxide catalysts due to sulfate ion leaching or the thermal 55 instability of the catalysts has been discussed in several other studies.<sup>31</sup> The post-treatment of catalysts to remove humins might also be responsible for sulfate ion removal on the metal oxide surface due to thermal decomposition. Ultimately, synthesized acidic TiO2 nanoparticles showed superior behavior in preserving 60 activity and thermal stability.



Fig.2 Reusability of TiO<sub>2</sub> nanoparticles and sulfated metal oxides. The catalysts were calcined at 400 °C for 1 h before reuse except the one for TiO<sub>2</sub> nanoparticles without calcination (▼) and calcined at the 6th use (◆ 65). (*Reaction conditions:* 20 mL 0.05 M fructose in MeOH, 0.1 g catalyst, 175 °C, 1 h.)

#### 4. Conclusions

In summary, we report a one-step synthesis of acidic TiO<sub>2</sub> 70 (anatase) nanoparticles that can produce high yields of ML in MeOH from different biomass derived carbohydrates under moderate conditions. The ML yields obtained from fructose were as high as 80 % with 80 % selectivity. Moreover, HMF, HMFderived ethers and higher molecular weight levulinic esters can 75 also be obtained by changing solvent feeds. Remarkable catalytic activity of the nanoparticles is attributed to *in-situ* sulfation on the surface and their superior dispersion in reaction media. These novel catalytic nanoparticles allow for the conversion of biomass derived carbohydrates efficiently at low temperatures ranging from 150 to 200 °C. The catalysts also show high recyclability with a minor loss of performance. These newly discovered acidic  $_5$  TiO<sub>2</sub> nanoparticles for biomass conversion open up a new avenue

of cost effective biomass refinery processes toward the production of affordable bio-chemicals and biofuels.

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#### Notes and references

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- <sup>20</sup> † Electronic Supplementary Information (ESI) available: Characterizations details of TiO<sub>2</sub> nanoparticles, including XRD diffractograms, SEM and TEM images, FT-IR spectra, NH<sub>3</sub>-TPD analysis, and TGA analysis. Experimental details, effect of catalyst loading on conversion of fructose, effect of time on conversion of <sup>25</sup> gulcose, and NMR spectrum of reaction products. See DOI: 10.1039/b000000x/
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