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# Catalytic Deoxygenation of Bio-Oil Model Compounds over Acid-Base Bifunctional Catalysts

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**ABSTRACT:** An acid-base bifunctional catalyst was synthesized by treating a natural mixed metal oxide, serpentine, with sulfuric acid. Catalyst characterization revealed the number of acidic and basic sites increased after the acid treatment largely due to an increase in surface area. However, stronger acid sites were also introduced by the formation of bridged hydroxyl groups between a Si atom and a heteroatom, as inferred by H NMR and NH<sub>3</sub>-TPD analysis. Results from SEM-EDS and H NMR suggested the acid and base sites were in close proximity. Catalytic conversions of carbohydrate-derived bio-oil model compounds were performed over different acid/base catalysts. Eight single bio-oil model compound and two binary mixtures were used. Reactivity of the model compounds was found to be strongly correlated to the number of oxygen containing functional groups in the reactant. The results from the binary mixtures showed the acid-base bifunctional catalyst had the highest activity in aldol condensation reactions. The best deoxygenation performance was also observed with the bifunctional catalyst for the model compounds were proposed based on an isotope labeling study. Deoxygenation reactions were found to be promoted by the cooperative catalysis between closely located acid and base sites.

**KEYWORDS:** acid-base bifunctional catalyst, bio-oil model compounds, catalytic pyrolysis, deoxygenation, mixed metal oxides

# **1. INTRODUCTION**

Fast pyrolysis is a promising technology, which can convert renewable biomass into liquid products, called bio-oil.<sup>1,2</sup> However, bio-oil has some important disadvantages relative to traditional hydrocarbon fuels primarily due to its high oxygen content,<sup>2-5</sup> which leads to low energy density, instability and corrosivity. Therefore, catalytic upgrading is necessary to diminish the excessive oxygen to create a viable liquid energy source. To alleviate the complexity involved in catalytic pyrolysis of biomass, many researchers have focused on upgrading bio-oil model compounds to build mechanistic insights of the upgrading process. Extensive studies have been performed for hydrodeoxygenation of bio-oil model compounds.<sup>6-14</sup> Relatively fewer studies were performed examining catalytic upgrading of bio-oil model compounds under pyrolysis conditions without adding any hydrogen, with zeolites have receiving the most attention.<sup>15-22</sup> Typical model compounds used includes furans, acids, esters, ketones, alcohols, phenols, etc.

Generally, similar types of aromatic and olefin species were observed as products from the catalytic conversion of bio-oil model compounds using different zeolites suggesting that common intermediates are involved in this process. Catalysis on acid sites and size-selectivity of the zeolite

dictates the product distribution. The proposed mechanism is the hydrocarbon pool theory,<sup>18,23,24</sup> in which the oxygenates diffuse into zeolite channel and undergo a series of reactions to remove oxygen in terms of CO, CO<sub>2</sub> and H<sub>2</sub>O, ending up with hydrocarbons and coke. Different reactivity for model compounds was reported as phenols had lower conversion than acids, esters, ketones and alcohols.<sup>19</sup> Although the monoaromatics and olefins produced from the zeolite catalysts can be used as petrochemicals, large amounts of less valuable polyaromatics were also formed.<sup>18,25,26</sup> Co-feeding of the model compounds with chemicals having a higher energy content was reported as a way to improve the hydrocarbon yield and the selectivity toward monoaromatics. A higher yield of aromatics and olefins was reported by co-feeding furans with methanol.<sup>20</sup> A synergistic effect between the reactants was proposed to promote methanol to olefins, Diels-Alder, and alkylation reactions. Similarly, higher selectivity towards xylene and toluene was reported by co-feeding furans with propylene through Diels-Alder reactions.<sup>21</sup> Graca et. al. found co-feeding of these model compounds, resulting in a higher yield of hydrocarbons and less coke formation. However, economic concerns need to be addressed due to the increased cost for co-feeding.<sup>22</sup>

In addition to zeolites, other catalysts were studied for upgrading bio-oil model compound in condensed phase reactions under elevated pressure without added hydrogen. Kunkes et al. reported catalytic conversion of glucose and sorbitol to monofunctional hydrocarbons and fuels through cascade flow reactors with different catalysts in each reactor.<sup>27</sup> The pressure used for these reactors ranged from 5 to 55 bar. Pt-Re/C was used in the first reactor to produce hydrogen and chemicals with a single oxygen functional group through C-C and C-O bond scission. The produced hydrogen was consumed in the following reactor where  $CuMg_{10}Al_7O_x$ ,  $Pd/CeZrO_x$ , and  $CeZrO_x$  were used as catalysts for hydrodeoxygenation, aldol condensation, ketonization, etc, to tune the final product distribution. To remove oxygen and create longer chain chemicals out of small aldehydes and ketones in bio-oil, Snell et al. examined aldol condensation of acetaldehyde, acetone and methyl ethyl ketone in a batch reactor pressurized to 350 psig at 150 °C over aluminum phosphate, known as an acid-base bifunctional catalyst.<sup>28</sup> It was proposed that under the reaction condition, acid and base sites were both necessary for aldol condensation.

To date, except for zeolites, few studies were performed involving upgrading of bio-oil model compounds under *in situ* fast pyrolysis conditions. Acid and base catalysts have been examined for their efficacy in oxygen removal during biomass fast pyrolysis since they can catalyze C-O and C-C bond cleavage through dehydration, decarboxylation and decarboxylation reactions.<sup>29-33</sup> While it is known that oxygen atoms in bio-oil are removed in the form of CO, CO<sub>2</sub> and H<sub>2</sub>O, the detailed reaction pathways are not clear due to the inherent complexity of this process. Acid-base bifunctional catalysts have been proposed to facilitate carbon-carbon bond forming reactions, which could help preserve carbon from small molecules by forming larger and more stable molecules.<sup>28,34-37</sup> Carbon-carbon bond forming reactions are typically accompanied with dehydration, which further contributes to oxygen removal. Therefore, acid-base bifunctional catalysts might be promising for upgrading bio-oil model compounds, since small molecules would be formed by the C-O and C-C cleavage promoted by acid or base sites and larger molecules generated by condensation reactions. To our knowledge, acid-base bifunctional catalysts have not been investigated for catalytic deoxygenation of bio-oil model compounds under fast pyrolysis conditions.

In the current study, acid, base and acid-base bifunctional catalysts were systematically examined for catalytic conversion of bio-oil model compounds at typical fast pyrolysis conditions in a fixed bed flow reactor. Silica-alumina and sulfated zirconia (a strong acid) were chosen as the

 acidic catalysts while MgO was chosen for the basic catalyst. The acid-base bifunctional catalyst was prepared by acid treatment of a naturally abundant serpentine mineral, which is a group of rock-forming hydrous magnesium iron phyllosilicate ((Mg, Fe)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) minerals commonly used as a source for magnesium. It has been reported that acid treatment can change the textural properties of serpentine, forming a high surface area material with increased accessibility to the active metal sites.<sup>38-45</sup> Since acid treatment can introduce acidic sites and leach out basic metals, the relative acidity versus basicity could be tuned by the extent of the acid treatment. Eight major products from carbohydrate pyrolysis, including acetaldehyde, acetone, acetol, methylglyoxal, methyl vinyl ketone, furfural, 5-methyl furfural and 5-hydroxymethylfurfural (HMF), were chosen as representative model compounds. Additionally, two aldol condensation reactions were examined as carbon-carbon forming reactions using two binary reactant mixtures, formaldehyde/acetaldehyde and formaldehyde/acetone. The overall scheme of the catalytic conversions is shown in Figure 1.



Figure 1. Scheme of catalytic deoxygenation of bio-oil model compounds.

# 2. EXPERIMENTAL SECTION

**2.1. Catalyst Preparation.** Information on the reactant chemicals is given in the supporting information. The as-received silica-alumina (grade 135) from Sigma-Aldrich contained 75 wt% silica, 13 wt% alumina and 11 wt% volatiles. Synthesis of the sulfated zirconia was performed using the method of Hino and Arata.<sup>46</sup> Zirconium (IV) hydroxide was added into 1M sulfuric acid with a weight ratio of 1 to 15. The solution was stirred for 1 h at room temperature followed by centrifugal separation. The solid was then dried at 110 °C for 2 h and calcined at 500 °C for 3 h. High surface area magnesium oxide (MgO) was prepared according to Bartley et. al.<sup>47</sup> Commercially available magnesium carbonate was calcined in air ramping from 25 °C to 550 °C at a rate of 10 C/min and then held at 550 °C for 2 h. The solid residue, which was MgO, was stored in a desiccator. Serpentine was provided by the Iowa State University Geology Department in a polymorph of chrysotile. The serpentine was ground using a ball mill into a fine powder. Acid treatment of the serpentine was performed using the method of Teiret. al.<sup>40,44,45</sup> The ground serpentine was added into a sulfuric acid solution using 1 to 10 weight ratio. Four sulfur acid concentrations, 1M, 1.5M, 2M and 3M, were used. The solution was stirred for 0.5 h at room temperature. The residue solid was then separated by centrifugation followed by copious washing with DI water until the pH value of the effluent was 7. The solid was then dried at 110 °C for 2 h and stored in a desiccator.

**2.2. Catalyst Characterization.** Surface area, pore volume and pore size distribution of the catalysts were analyzed using nitrogen physisorption. Induced-coupled plasma mass spectrometry (ICP-MS) was used to analyze metal content in the serpentine materials before and after acid

treatment. Elemental analysis was performed with an Elementar Vario Micro cube to quantify the C, H, N, S content in the serpentine samples. X-ray photoelectron spectroscopy (XPS) was performed to quantify the surface composition of the serpentine samples. For x-ray diffraction (XRD) measurement, a Scintag XDS-2000 was used. <sup>1</sup>H NMR spectra were taken using a Bruker Advance 600 spectrometer. A FEI Quanta FE-SEM was used to obtain scanning electron micrographs (SEM) of the materials and was connected to an energy dispersive X-ray spectroscope (EDS) from Aztec Oxford Instruments. Temperature programmed desorption (TPD) was used to characterize the acid and base sites on the catalysts. Details for catalyst characterization are given in the supporting information.

**2.3.** Isotope Labeled HMF Synthesis and Tracking. For insights on reaction pathways in the catalytic conversion of HMF, isotopically labeled HMF was used. The isotope labeled HMF was synthesized from D-glucose-1-<sup>13</sup>C and D-glucose-6-<sup>13</sup>C in a biphasic solvent system according to the method of Wang et. al.<sup>48</sup> A 5 mmol/L alumina chloride aqueous solution was saturated with sodium chloride to create an acidic solution and then 100 mg of labeled glucose and 3 g tetrahydrofuran (THF) were added into 1.5 g of the acidic solution in a batch reactor. The reactor was sealed and placed in an oil bath, which was preheated to 155 °C. The reaction solution was stirred for 90 min resulting in a biphasic solution, where HMF and THF were in the nonpolar phase layer with the acid and unconverted glucose in the aqueous phase. The nonpolar phase was removed and dried in an oven at 40 °C to separate by evaporation THF from the HMF. The purity of the synthesized isotopically-labeled HMF was quantified using a micro-reactor system described below giving a value of 78 wt% after vaporization at 300 °C. Details on the characterization of the synthesized HMF are given in the supporting information.

The catalytic conversion of the isotope-labeled HMF is described in section 2.4. The mass spectra of the conversion products from the HMF were used to analyze the <sup>13</sup>C distribution. The relative intensities of the molecular ions with or without <sup>13</sup>C were deconvoluted in consideration of the proton loss contribution.<sup>49,50</sup> The contribution of the M+1 peak, which was derived from the presence of natural <sup>13</sup>C, was also considered. For a single product, the relative intensities of the deconvoluted molecular ions without <sup>13</sup>C, with one <sup>13</sup>C, and with more <sup>13</sup>C atoms were used to determine their relative mole percentage abundance. During the calculation, standard mass spectra form the NIST database for the pure chemicals were used.

2.4. Catalytic Conversion. Catalytic conversion of the bio-oil model compounds over acidic, basic, bifunctional and physical mixtures of acidic and basic materials was investigated using a Tandem micro-reactor system (Rx-3050 TR, Frontier Laboratories, Japan) under atmospheric pressure.(shown in Figure S1) The first reactor held at 300 °C was used to vaporize the liquid or solid reactant. The vapor was swept by continuous He flow to the second reactor, which contained the catalyst. The temperature of the second reactor was set typical fast pyrolysis temperatures of either 445 °C or 500 °C. A fixed catalyst bed was packed inside a quartz tube in the second reactor. To prevent bypass flow, the particle size in the quartz tube was kept smaller than 1/10 of the tube diameter and the length of the fixed bed was adjusted to 5 times the tube diameter by mixing catalyst particles with acid washed sand, which was proven to be inert during catalysis. Both the catalyst pellets and inert sand particles were sieved to 50 - 70 mesh size and the bed was immobilized by quartz wool placed at both ends of the quartz tube. There were two interfaces in the micro-reactor system. The first was between the two reactors and the second was between the second reactor and the GC. The temperature for both interfaces was kept at 300 °C to minimize condensation of products. The products formed during the reaction were analyzed online by GC (7890A, Agilent Technologies, USA), which was equipped with three detectors. A

three-way splitter in front of the columns enabled simultaneous analysis by the three detectors. A MS was used for product identification. The FID was used to quantify the condensable products and the TCD was used to quantify non-condensable gas, such as CO,  $CO_2$  and olefins. Coke yield was measured by introducing air into the catalyst bed at 550 °C and quantifying CO and  $CO_2$  from the combustion. Details of the temperature ramping program and calibration methods are given in the supporting information.

The model compounds used included acetaldehyde, acetone, acetol, methylglyoxal, methyl vinyl ketone, furfural, 5-methylfurfural and HMF. Moreover, two binary mixtures, formaldehyde/acetaldehyde and formaldehyde/acetone, were also used to examine aldol condensation. Given the 37 wt% purity for formaldehyde, a volume ratio of 3:1 was applied for the formaldehyde and acetaldehyde mixture as well as formaldehyde and acetone mixture to roughly obtain 1:1 molar ratios for the reactants. The amount of reactant used was 0.4 mg for a single model compound and 1 µl for the binary mixture. To deal with deactivation, the catalyst to reactant mass ratio was kept larger than 10 for serpentine. Loading for the other catalysts was calculated based on the serpentine loading to ensure the same total number of acid and/or basic sites for each experiment. All experimental results were based on the average value of triplicate runs. Negligible change in the product yields were observed during the triplicate runs. For the catalytic conversion of a single compound, the product distribution was reported as carbon yield, which was defined as moles of carbon in the product divided by the moles of carbon in the reactant. The selectivity was defined as the carbon yield of a specific product divided by the reactant conversion. For aldol condensation between formaldehyde and acetaldehyde, the product yield was reported as moles of propenal formed divided by moles of acetaldehyde in the reactant mixture. For aldol condensation between formaldehyde and acetone, product yield was reported as moles of methyl vinyl ketone formed divided by moles of acetone in the reactant mixture. In this work, deoxygenation performance was evaluated based on the overall yield and average oxygen content of deoxygenation products.

# **3. RESULTS AND DISCUSSION**

**3.1. Catalyst Characterization.** The nitrogen adsorption-desorption results for the different catalysts are shown in Table 1. Pore volumes were obtained at P/Po = 0.97, representing pores with diameter less than 75 nm, and the average pore size was calculated based on the BJH desorption curve. The type IV adsorption and desorption isotherm curves (Figure S2) for the serpentine materials indicated mesoporous structures. After acid treatment, the BET surface area was 30 times higher and pore volume 10 times higher than the starting material. Moreover, after acid treatment a considerable amount of microporosity was generated and the average mesopore size decreased, so the treatment led to the formation of micropores and small mesopores. As shown in Table 1, the different  $H_2SO_4$  acid treatment concentrations did not significantly alter the textural properties.

Table 1. Textural properties for ground serpentine	, acid-treated serpentine,	silica-alumina,
sulfated zirconia and MgO		

	0			
catalyst	BET surface area (m <sup>2</sup> /g)	pore volume (cm <sup>3</sup> /g)	T-plot micropore volume (cm <sup>3</sup> /g)	BJH average pore size (nm)
ground serpentine	16.6	0.045	~0	18.70
serpentine1M <sup>a</sup>	570.7	0.546	0.039	5.05

.: on ch	456.0	0.450	0.044	6.20
serpentine3M°	456.8	0.458	0.041	6.20
silica-alumina	519.9 <sup>c</sup>	-	-	-
sulfated zirconia	85.4	-	-	-
MgO	161.5	0.235	0.004	4.74
	L-			

<sup>*a*</sup> serpentine treated with 1M  $H_2SO_4$ ; <sup>*b*</sup> serpentine treated with 3M  $H_2SO_4$ ; <sup>*c*</sup> from provider.

	Table 2. Bulk compositi	on (wt%) of se	rpentine sam	ples from ICP-MS an	d elemental analysis
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catalyst	Mg <sup>a</sup>	$AI^{a}$	Ca <sup>a</sup>	$Fe^{a}$	S <sup>b</sup>	$H^{b}$	C <sup>b</sup>	$N^{b}$	total metal
serpentine	24.07	0.12	4.07	3.34	0.03	0.61	2.19	0.01	31.60
serpentine 1M <sup>c</sup>	6.09	0.11	0.06	6.35	0.10	-	0.06	0.01	12.61
serpentine 1.5 M <sup>d</sup>	1.44	0.01	0.13	2.31	-	-	-	-	3.89
serpentine 2M <sup>e</sup>	1.06	0.01	0.11	1.97	-	-	-	-	3.16
serpentine3M <sup>f</sup>	0.65	0.01	0.60	1.54	3.33	1.35	0.14	0.01	2.37

<sup>*a*</sup> data from ICP-MS; <sup>*b*</sup> data from elemental analysis; <sup>*c*</sup> serpentine treated with 1M H<sub>2</sub>SO<sub>4</sub>; <sup>*d*</sup> serpentine treated with 2M H<sub>2</sub>SO<sub>4</sub>; <sup>*f*</sup> serpentine treated with 3M H<sub>2</sub>SO<sub>4</sub>.

#### Table 3. Serpentine surface compositions (wt%) from XPS.

catalyst	C1s	O1s	Mg2p	Al2p	Si2p	S2p	Ca2p	Fe2p	total metal	
serpentine	5.10	57.87	15.95	< 0.10	16.88	0.28	3.83	2.82	22.60	
serpentine 1M	4.15	56.39	4.31	< 0.10	28.84	0.67	0.15	5.50	9.95	
serpentine 1.5 M	2.92	58.58	0.55	< 0.10	35.23	1.41	0.17	1.14	1.86	
serpentine 2M	4.67	57.72	0.48	< 0.10	35.46	1.34	0.03	0.30	0.81	
serpentine 3M	4.22	56.50	0.37	< 0.10	30.70	3.99	0.30	0.12	0.78	

The approximate composition of serpentine is  $Mg_3Si_2O_5(OH)_4$ , which could vary by its origin and polymorph form.<sup>51</sup> The bulk and surface composition of the serpentine samples are shown in Tables 2 and 3, respectively. The metal content trend versus acid treatment concentration was consistent between the bulk and surface. Apparent leaching occurred for Mg and Ca during acid treatment as the Mg content decreased with increasing acid concentration, while Ca content decreased to a very low level. In contrast, the Fe content first increased and then decreased with increasing acid concentration suggesting Fe was less prone to leaching. Overall, the total metal content decreased with increasing acid concentration. In contrast, the surface and bulk sulfur content increased with increasing acid concentration. The hydrogen content also increased after treatment with  $3M H_2SO_4$ , suggesting hydroxyl groups were introduced during the acid treatment. Considering silicic acid is synthesized by acidification of silicate salts, the hydroxyl groups were probably in the form of silanols.

Figure 2 shows XPS scans of the serpentine materials within the specific range of binding energies representing Mg2p, Ca3s, Ca2p, S2p and Si2p. Integration of these peaks provided their surface composition, as shown in Table 3. Oxidation state and chemical bonding was determined by binding energy shifts referenced to the NIST database. Serpentine had a wide Mg2p peak centered at 51 ev, consistent with magnesium silicates that range from 50.46 to 51.15 ev.<sup>52,53,54</sup> After acid treatment, the Mg2p peak was shifted to 49.5 - 50.25 ev, which could be attributed to

 MgO formation.<sup>55</sup> MgSO<sub>4</sub> might also be formed given the wide S2p peak centered at 169.5 ev.<sup>56</sup> Ca seemed to primarily be in the CaO form for serpentine as the Ca3s peak was at 45 - 45.5 ev.<sup>57</sup> The peak shifted to 44.5 - 45 ev after acid treatment, which was consistent with partial conversion of CaO to CaSO<sub>4</sub>.<sup>58</sup> The formation of CaSO<sub>4</sub> was also evident by the presence of a Ca2p peak centered at 348.25 ev<sup>59</sup> and a S2p peak centered at 169.5 ev.<sup>60,61</sup> Taken together, the acid treatment appeared to partially convert the magnesium silicate and CaO in serpentine into MgO, MgSO<sub>4</sub> and CaSO<sub>4</sub>, respectively.



**Figure 2.** XPS scan for serpentine before and after acid treatment (vertical axis is counts per second). (a) Mg2p and Ca3s, (b) Ca2p, (c) S2p, (d) Si2p.

Figure 3 and Table 4 give the results for the acidity/basicity measurements with the serpentine samples. After acid treatment, both the acid amount and strength increased. Generally, the acid amount and strength seemed proportional to the acid concentration used. The changes in acidity were not attributed to residual sulfuric acid, since reproducible chemisorption results were observed after heat treatment at 600 °C, which was well above the sulfuric acid decomposition temperature. The acidity increase could be explained by two factors; a) a significant increase in the surface area after acid treatment leading to an increase in the number of acid sites and b) silanol and sulfur groups were introduced, as suggested by the increased H and S content (Table 2), which would increase acid strength and the number of acid sites. This proposed explanation will be further discussed in the H NMR section. During chemisorption, the desorbing gas was analyzed by MS to confirm the peaks shown in Figure 3 were NH<sub>3</sub> (TPD-MS results shown in Figure S3).

The sulfated zirconia as seen in Figure 3 exhibited strong acid sites represented by two peaks around 395 °C and 865 °C, which confirmed the successful synthesis of the solid acid.<sup>62</sup> For silica-alumina a wide peak ranging from 100 to 540 °C was observed, which was in a similar range as the acid-treated serpentine. Therefore, the acidic strength of silica-alumina appeared to be comparable to the acid-treated serpentine.

The overall basicity also increased after acid treatment since the number of basic sites was strongly correlated to the surface area. In contrast to the acidity measurement, the base amount first increased and then decreased with increasing acid concentration likely due to increased metal leaching with the more concentrated acid treatments. For the serpentine materials, the magnesium appeared to be the basicity source since the position of the base peak matched that of MgO. Ca and Fe might have also contributed to the basicity but appeared to play a weaker role. The 1M treated serpentine had more basic sites than serpentine treated by 1.5M- 3M acid apparently due to the balance between surface area and metal leaching.



**Figure 3.**  $NH_3$ -TPD acidity measurement; (a) serpentine materials, (c) acid catalysts and  $CO_2$ -TPD basicity measurement (b) serpentine materials, (d) MgO.



**Figure 4.** <sup>1</sup>H NMR Hahn-echo spectrum of (a) serpentine, (b) serpentine 1M, and (c) serpentine 3M.

The NMR spectra for serpentine before and after acid treatment are shown in Figure 4. The two large peaks around 1.1 ppm and 0.8 ppm represented isolated silanols<sup>63,64</sup> and silanol groups interacting with oxygen in the framework,<sup>65,66</sup> respectively. Both peaks have been reported to be non-acidic. A small peak at 1.8 ppm was observed for serpentine and serpentine 1M, which has been attributed to weakly acidic terminal silanols.<sup>67,68</sup> An apparent peak shoulder around 2.1

 ppm was observed for the serpentine 1M (Figure 4(b)). The shoulder has been ascribed to internal silanol groups that are strongly acidic.<sup>67</sup> Additionally, the peak observed at 5.1 ppm in Figure 4(b) and not 4(a) could be attributed to bridged hydroxyl groups. These bridged hydroxyls are between a Si atom and a heteroatom, such as Al for zeolites.<sup>63,65,67</sup> For serpentine, the heteroatom might be Fe, Mg or Ca. These bridged hydroxyls have been proposed to be strong acid sites.<sup>63,65,67</sup> NH<sub>3</sub>-TPD results demonstrated after acid treatment that both the number of acid sites and acid strength increased. The peak at 5.1 ppm and peak shoulder around 2.1 ppm in serpentine 1M inferred the presence of a stronger acid site after acid treatment. The increase of weak acid sites was evident from peak integration at 1.8 ppm, which showed the intensity of this peak was three times larger in Figure 4(b) than 4(a). For serpentine 3M, peaks representing weak acids and strong acids overlapped, due to a significant increase on both weak and strong acid sites.

### Table 4. Total acid/base amount for the different catalysts

	serpentine	serpentine	serpentine	serpentine	serpentine	silica-	sulfated	MgO
		1M	1.5M	2M	3M	alumina	zirconia	
total acid amount (mmol/g)	0.049	0.144	0.133	0.145	0.270	0.577	0.270	-
total base amount (mmol/g)	2.02	7.79	5.37	4.98	4.60	-	-	23.88

SEM images for the serpentine before and after acid treatment are shown in Figure S4. It can be seen that acid treatment led to the formation of a coral-like porous agglomerate consisting of smaller particles apparently resulting from corrosion or dissolution by the sulfuric acid.



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**Figure 5.** EDS spectrum for serpentine materials; (a) overall spectra, (b) Fe and Mg rich spots on serpentine 1M, (c) Fe/Mg and S rich spots on serpentine 3M.

Figure 5 and Table S1 give the EDS spectra and composition of the serpentine samples. The compositional change with acid treatment was consistent with the results from ICP and XPS. Areas enriched with specific elements were found in SEM-EDS image within a diameter of less than 1  $\mu$ m, as shown in Figure S5. The spectra for these metal and sulfur rich areas are also shown in Figures 5(b) and (c). As can be seen, the Mg and Fe rich spot for the acid treated serpentine also contained a large amount of Si and O, which was consistent with the existence of bridged hydroxyls seen in the H NMR analysis. Also, Figure 5(c) shows the S rich area contained a considerable amount of Ca and Mg. Combined with XPS, the results suggested the possible formation of sulfur-promoted metal oxides in serpentine 3M, which would be highly acidic. The SEM-EDS maps for the distribution of Mg, Fe, S, Si and O in serpentine materials are shown in Figures S6 to S10 in the supporting information.

XRD results for the serpentine samples are shown in Figure S11 using CaO as the internal standard. The broad peak ranging from 5 to  $25^{\circ} 2\theta$  suggested a somewhat amorphous structure

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for the serpentine materials. The center of the broad peak around 13°  $2\theta$  was consistent with the characteristic peak for serpentine.<sup>69,70</sup> Peaks at 32.4, 37.5 and 54.1°  $2\theta$  were from the internal standard. Comparison before and after treatment suggested acid treatment did not further change the crystalline structure.

**3.2. Aldol Condensation Test.** As shown in Figure 6, two aldol condensation reactions were examined, propenal formation from formaldehyde/acetaldehyde and methyl vinyl ketone formation from formaldehyde/acetone. The experiments were performed by feeding the chosen mixture over the different catalysts. For each catalyst, both high and low catalyst loadings were used. The same number of acid sites and/or base sites among the different catalysts was maintained for each catalyst loading level. The reaction results are shown in Figure 7, with the molar yield of propenal based on acetaldehyde conversion and molar yield of methyl vinyl ketone on acetone conversion. In the current work, MgO was chosen to represent a base catalyst due to its similar basic strength as the serpentine 1M. For the acid catalysts, both the sulfated zirconia and silica-alumina were chosen to examine the influence of acid strength on aldol condensation.

**Figure 6.** Aldol condensation from (a) formaldehyde and acetaldehyde (b) formaldehyde and acetone.

As shown in Figure 7, aldol condensation occurred with all of the catalysts. The serpentine 1M showed the highest yield for both reactant mixtures. The base case without a catalyst gave less than 1 % of the aldol condensation product. For both reactions the product yield increased with higher catalyst loading. The acid strength did not significantly affect either reaction as seen by comparing the sulfated zirconia with the silica-alumina. A physical mixture of MgO/sulfated zirconia enhanced the aldol condensation reaction compared to the individual acid or base catalyst, but was still inferior in activity to the serpentine 1M. Based on the results in Figure 7, turnover frequencies were calculated for the catalysts at two loadings, using Equation (1) in the supporting information. For the calculation, the moles of product formed by aldol condensation was divided by the moles of active sites (either acid or base) and residence time. The residence time was calculated by using an experimentally measured void volume for the catalyst bed divided by the flow rate. As shown in Table 5, each catalyst had similar TOF values for the given reaction at the different loadings, suggesting the absence of transport limitations in the experiments.<sup>71,72</sup> As seen in the table the acid-base bifunctional catalyst was more active for aldol condensation than the individual acid or base catalysts.

Aldol condensation is an addition reaction, for which the formation of a protonated carbonyl could be catalyzed by an acid site that acts as the electrophile, while the formation of a deprotonated enolate could be catalyzed by a base site acting as a nucleophile. Therefore, in the presence of an acid-base co-catalyst both electrophilic and nucleophilic addition could be promoted due to presence of each.<sup>35</sup> Moreover, the higher TOF for the serpentine 1M than the acid/base catalyst physical mixture suggested the presence of adjacent acid and base sites facilitated the reaction. H NMR and SEM-EDS analysis suggested the existence of bridged hydroxyls on serpentine 1M where the H could act as the acidic site, while the metal oxides bridging the hydroxyls could act as the basic site. A carbon balance calculation showed less than 10 %

unaccounted for carbon after the reaction for all cases, which was probably due to coke formation as deposited carbon was found on the postreaction catalysts.



**Figure 7.** Molar yield of aldol condensation products; (a) methyl vinyl ketone formation from formaldehyde and acetone, (b) propenal formation from formaldehyde and acetaldehyde. Reaction conditions: vaporization temperature = 300 °C; catalyst temperature = 445 °C; flow rate = 10 ml/min; reactant loading = 1 µl; high catalyst loading: 7.5mg serpentine 1M, 2.7 mg MgO, 3.6 mg sulfated zirconia, 1.7 mg silica-alumina; low catalyst loading: 3.6 mg serpentine 1M, 1.3 mg MgO, 1.7 mg sulfated zirconia, 0.8 mg silica-alumina; MgO/sulfated zirconia: physical mixture of MgO and sulfated zirconia.

		prop	enal		methyl vinyl ketone					
	TOF/a	cid(s <sup>-1</sup> )	TOF/ba	ase(s <sup>-1</sup> )	TOF/a	cid(s <sup>-1</sup> )	TOF/base(s <sup>-1</sup> )			
catalyst	high Ioading <sup>a</sup>	low loading <sup>b</sup>								
serpentine 1M	7.61	6.25	0.137	0.112	1.93	1.91	0.035	0.034		
MgO	-	-	0.045	0.041	-	-	0.025	0.028		
sulfated zirconia	1.66	1.50	-	-	0.57	0.60	-	-		
Silica-alumina	1.58	2.09	-	-	0.70	1.04	-	-		
MgO/ sulfated zirconia	3.67	3.81	0.066	0.070	1.69	1.80	0.030	0.033		

Table 5. Turnover free	quencies for pro	penal and methy	yl viny	I ketone formation.

<sup>a</sup>7.5 mg serpentine 1M, 2.7 mg MgO, 3.6 mg sulfated zirconia, 1.7 mg silica-alumina; <sup>b</sup>3.6 mg serpentine 1M, 1.3 mg MgO, 1.7 mg sulfated zirconia, 0.8 mg silica-alumina.

To investigate the influence of relative acidity versus basicity, the aldol condensation reaction was performed over the same amount of serpentine materials treated by different acid concentrations. Figure 8 shows the product yield from aldol condensation for these catalysts. A different trend was observed for the two reactions. As seen in Figure 8 when referenced to Table 4, the propenal yield decreased from serpentine 1M to serpentine 2M, which corresponded to a decreasing number of basic sites with comparable acidic sites. However, a higher yield of propenal was observed for serpentine 3M compared to serpentine 2M, with the acid amount of the former being twice as much while only having 8% fewer basic sites. Therefore, both the acid and base site amounts on the catalysts influenced propenal formation with the highest propenal yield observed using the serpentine 1M catalyst. In contrast, a monotonic reduction in methyl vinyl ketone yield

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was observed from serpentine 1M to serpentine 3M, suggesting the catalysis was limited by the number of basic sites. Propenal formation was from two aldehydes, while methyl vinyl ketone formation involved a ketone as a reactant. Compared to acetaldehyde, the hydrogen on the  $\alpha$  carbon in acetone is less acidic due to an electron donating methyl group attached to the carbonyl, resulting in more difficulty to form a deprotonated enolate. In this case, enolate formation was more likely to be catalyzed by the original basic site instead of the conjugated base from the acid.<sup>73</sup> Therefore, base catalysis to form the enolate could reasonably be the rate limiting step to produce methyl vinyl ketone.



**Figure 8.** Molar yield of aldol condensation products; (a) propenal formation from formaldehyde and acetaldehyde, (b) methyl vinyl ketone formation from formaldehyde and acetone. Reaction conditions: vaporization temperature = °C; catalyst temperature = 445 °C; flow rate = 10 ml/min; reactant loading =  $1 \mu$ l; catalyst loading: 7.5 mg.

**3.3. Reactivity Testing for Bio-Oil Model Compounds.** Serpentine 1M was chosen as the acid-base bifunctional catalyst for examining the conversion of bio-oil model compounds. The reactivities of the model compounds were tested at 445 °C and 500 °C over the different catalysts with the results shown in Table 6. Acetaldehyde, acetone, methyl vinyl ketone, furfural and 5-methyl furfural showed relatively lower conversions compared to acetol, methylglyoxal and HMF. The reactivity was strongly correlated to the number of oxygen-containing functional groups in the reactant. For low molecular weight (LMW) compounds, both acetol and methylglyoxal have two oxygen containing functional groups while acetaldehyde, acetone and methyl vinyl ketone have only one. Similarly, for the furans, HMF has two oxygen containing functional groups not in the ring, while furfural and 5-methyl furfural have only one. It is reasonable to speculate that reactants with a higher number of oxygen containing functional groups have a stronger interaction with active sites on the catalysts.

	control		serpentine 1M		silica-a	silica-alumina		sulfated zirconia		MgO		alumina+MgO		MgO	
model compounds	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	
acetol	6.8		100.0	100.0	83.8	99.1	75.7	96.4	55.3	88.9	87.1	99.3	94.9	100.0	
methylglyoxal	3.7		59.5	61.5	58.7	57.0	46.5	49.6	50.1	50.6	55.7	53.6	48.0	60.6	
HMF	2.0		100.0	100.0	93.1	91.7	83.7	98.3	71.4	86.7	84.9	98.2	77.8	75.4	
acetaldehyde	<1		<1	10.5	-	-	<1	<1	<1	<1	<1	<1	<1	<1	
acetone	<1		12.7	4.1	<1	<1	<1	<1	<1	<1	<1	2.1	<1	<1	

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methyl vinyl ketone	1.7	18.2	21.7	-	-	3.7	-	8.0	-	18.2	16.3	4.6	3.6
furfural	<1	4.6	4.8		-	<1	-	1.4		-	-	<1	4.6
5-methyl furfural	<1	10.0	14.9	-	-	<1	-	<1	-	15.5	16.8	<1	<1

<sup>*a*</sup>Values are in mol%, reaction conditions: vaporization temperature = 300 °C; catalyst temperature = 445 °C or 500 °C; flow rate = 90 ml/min; reactant loading = 0.4 mg or 0.4  $\mu$ l; catalyst loading: 17 mg for serpentine 1M, 4.2 mg for silica-alumina, 9.0 mg for sulfated zirconia, 5.7 mg for MgO.

**3.4. Reaction Pathways for HMF Conversion.** Shown in Table 7 are the major products from the HMF conversion, which included 5-methyl furfural, 2,5-furandicarboxaldehyde, 2-methyl furan, furfural, CO and CO<sub>2</sub>, over the catalysts. Water was identified as a product by the online MS, but couldn't be accurately quantified. To better understand the reaction pathways involved in the reaction, isotope labeled HMF was used as the reactant. The C-1 and C-6 on the HMF molecule were selectively labeled with <sup>13</sup>C. The characterization of the 1-<sup>13</sup>C HMF and 6-<sup>13</sup>C HMF is described in Figure S12.

Table 7. Product distribution from catalytic conversion of HMF over different catalysts<sup>a</sup>

product	serpentine 1M		silica-a	lumina	M	gO	silica-alumina+ MgO	
	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C
furan	0.5	1.0	1.3	1.8	0.4	0.5	1.3	1.9
2-methyl furan	5.5	10.0	5.9	8.6	0.7	1.0	3.7	5.9
2,5-dimethyl furan	0.4	0.7	0.2	0.3	0.2	0.3	0.2	0.3
furfural	2.7	3.2	0.9	1.2	1.9	3.2	1.6	2.6
5-methyl furfural	30.7	26.3	23.0	23.5	20.3	24.9	12.7	13.5
2,5-Furandicarboxaldehyde	13.1	7.5	21.5	13.2	21.7	21.6	8.6	7.2
CO	3.6	8.0	4.7	7.3	1.2	2.6	3.9	6.1
CO <sub>2</sub>	3.3	4.7	2.1	2.2	0.9	1.5	1.2	2.4
unconverted HMF	0	0	6.9	8.3	28.6	13.3	15.1	1.8
coke <sup>b</sup>	-	36.6	-	17.7	-	25.4	-	43.0
carbon balance <sup>b</sup>	-	98.1	-	84.2	-	94.2	-	84.7

<sup>*a*</sup>All numbers are given as carbon % yield. Reaction conditions: vaporization temperature = 300 °C; catalyst temperature = 445 °C or 500 °C; flow rate = 90 ml/min; reactant loading = 0.4 mg; catalyst loading: 17 mg for serpentine 1M, 4.2 mg for silica-alumina, 5.7 mg for MgO. <sup>*b*</sup>Coke was only measured for catalysis at 500 °C and carbon balance was only shown for catalysis at 500 °C.

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**Figure 9.** Carbon source for products from conversion of isotope labeled HMF over serpentine 1M; (a) products with one carbon atom or five carbon atoms; and (b) products with four carbon atoms or six carbon atoms. Reaction conditions: vaporization temperature = 300 °C; catalyst temperature = 445 °C; flow rate = 90 ml/min; reactant loading = 0.4 mg; catalyst loading: 17 mg.



Figure 10. Distribution of labeled C in product from conversion of HMF over serpentine 1M.

The distribution of <sup>13</sup>C in the products from the catalytic conversion of isotope labeled HMF over serpentine 1M are summarized in Figure 9. The C-1 in the HMF molecule was significantly more involved in CO and  $CO_2$  formation than the C-6. Most of the 2-methyl furan contained the C-6 from HMF instead of the C-1, while most furfural contained the C-1 from HMF rather than the C-6. The 5-methyl furfural primarily contained one <sup>13</sup>C atom, either the C-1 or C-6 from HMF. The position of the <sup>13</sup>C in the 5-methyl furfural was determined by its mass spectra as shown in the supporting information. Similarly, the 2,5-furandicaboxaldehyde product contained one <sup>13</sup>C in the aldehyde group. Little <sup>13</sup>C labeled carbons were observed in the furan product. Taken together, the distribution of <sup>13</sup>C in the 5-methyl furfural, 2,5-furandicarboxaldehyde and furan products suggested the backbone of furan was not ruptured or rearranged during the reaction. This result would suggest no hydrocarbon pool mechanism where carbon atoms lose their identity as happens with zeolites. From the data in Figure 9, the distribution of labeled C was

consistent with the scheme in Figure 10. By stoichiometry, formaldehyde would be formed during furfural formation, which was supported by identification of formaldehyde in the mass spectra. Unfortunately, isotope tracking and quantification for formaldehyde were not successful due to peak overlap under the experimental conditions.



**Figure 11.** Catalytic conversion of HMF over different catalysts with same number of acid and/or basic sites at (a) 445 °C and (b) 500 °C. Reaction condition: same as Table 7; Yield is in terms of carbon yield; oxygen content in products is in wt%; products here refer to deoxygenation products as shown in Figure 1, not including CO,  $CO_2$  and  $H_2O$ .

As shown in Table 7, the deoxygenation products from the catalytic conversion of HMF were a mixture of furanic compounds. In this work, deoxygenation performance was evaluated based on the yield of deoxygenation products and the oxygen content in the products, as given in Figure 11. For both reaction temperatures, the acid or base catalysts resulted in a higher oxygen content in the products compared to serpentine 1M. The acid/base physical mixture showed a similar oxygen content in the products as the serpentine 1M, but had a lower yield for the deoxygenation products. The serpentine catalyst decreased the oxygen content in the product mixture by one fourth and the carbon yield of the product was 49 %. Unlike other catalysts, complete conversion was observed for serpentine 1M, suggesting it had higher activity for HMF conversion. The product distribution inferred a series of reactions occurred. The same types of products were observed over the different catalysts, suggesting the difference in deoxygenation performance was dictated by the relative activity of the different pathways, which are shown in Table S2 in the supporting information. The largest difference between acid catalysis (silicaalumina) and base catalysis (MgO) was that the latter had higher selectivity towards 2,5furandicarboxaldehyde formation and the former had higher selectivity towards 2-methyl furan formation. As suggested in Figure 10, 2,5-furandicarboxaldehdye was formed by the dehydrogenation of HMF, which is typically catalyzed by base catalysts.<sup>74-80</sup> The oxygen in the hydroxyl group could adsorb onto a magnesium ion to form an alkoxide followed by proton loss from the hydroxyl group. Formation of the alkoxide would create a negative charge on the alpha carbon, which would facilitate hydride formation from the alpha hydrogen. An adjacent magnesium ion could then be active in abstracting the alpha hydrogen as a hydride acceptor. Finally,  $H_2$  could be formed by a reaction between the hydride and a suitable proton. Abstraction of the oxygen from the magnesium ion would complete the formation of the carbonyl group. For 2-methyl furan formation, the isotopic labeling studies suggested fragmentation between the C-1

 and C-2 on the HMF molecule. As provided in Table S5, 2-methyl furan was shown to be formed from 5-methyl furfural. Therefore, the formation of 2-methyl furan was largely determined by the rate of decarbonylation. The higher selectivity towards 2-methyl furan for silica-alumina compared to MgO could be due to a higher activity for decarbonylation with the former. While a typical catalyst for decarbonylation is a transition metal complex,<sup>81,82</sup> acid catalysts, including zeolites and MCMs, have been reported to facilitate decarbonylation during biomass catalytic fast pyrolysis.<sup>18,25,26,83</sup> The formation of 5-methyl furfural may have utilized the hydrogen transferred during the formation of 2,5-furandicarboxaldehyde. As shown in Figure 12, the speculated pathway could involve elimination of the hydroxyl group on HMF by proton attack. Then, the intermediate carbocation abstracts one hydride ion formed during the dehydrogenation to generate 5-methyl furfural. As such, 5-methyl furfural formation could be facilitated by the cooperation of acidic and basic sites with the acid site providing the proton for hydroxyl elimination and the base site providing the hydride for the carbocation intermediate. This pathway was consistent with the higher 5-methyl furfural selectivity observed for the serpentine catalyst compared to the other catalysts. The one exception was MgO, whose higher 5-methyl furfural selectivity MgO could have resulted from a lower decarbonylation activity, which subsequently converted 5-methyl furfural to 2-methyl furan. Considering the oxygen content in the product distribution, the generation of 2-methyl furan and 5-methyl furfural contributed to lowering the average oxygen level of the product mixture. The selectivity for these two products was the highest for serpentine 1M and combined with its highest activity, led to the best deoxygenation performance.

More fragmentation occurred at higher reaction temperature (Table S2) as the selectivity towards furans with 4 or 5 carbon atoms increased. This trend was also evident in the higher selectivity towards CO and CO<sub>2</sub>. A small fraction of furfural decomposed to furan and CO under these conditions as shown in Table S6. Taken together, the reaction network could be illustrated by Figure 13. The basic sites appeared to promote HMF dehydrogenation to 2,5-furandicarboxaldehdye with the intermediate hydrogen ion formed during the dehydrogenation then participating in 5-methyl furfural formation. The acid sites appeared to facilitate decarbonylation to remove oxygen as CO. Formation of 5-methyl furfural required removal of oxygen as water, which might be facilitated by the synergetic effects between the acid and base sites. Therefore, cooperation between the acidic and basic sites seemed to facilitate oxygen removal by a series of reactions including dehydrogenation, dehydration and decarbonylation.

 $\underbrace{\overset{+H^+}{\longrightarrow}}_{-H_2O} \underbrace{\overset{+}{\longrightarrow}}_{-} \underbrace{\overset{0}{\longrightarrow}}_{-} \underbrace{\overset{0}{\longrightarrow}}_$ 

Figure 12. Speculated reaction pathway for formation of 5-methyl furfural.



**Figure 13.** Reaction network for catalytic deoxygenation of HMF over the acid/base catalyst (Carbon atoms are isotope labeled by asterisk).

**3.5. Reaction Pathways for Acetol Conversion.** The major products from acetol conversion (Table 8) over the catalysts were acetone, acetaldehyde, ethylene and methylglyoxal. Additionally, there were hydrocarbons formed, mainly ethylene. The total product yields and the calculated oxygen content in the product mixtures are shown in Figure 14. The highest product yield was achieved with serpentine 1M at both reaction temperatures and the oxygen content in the product was primarily the lowest, with an one third decrease after conversion at 500 °C. The highest activity was observed with serpentine 1M, while a relatively low activity was observed for MgO and sulfated zirconia. The higher performance with the serpentine 1M was primarily associated with the formation of olefins and acetone.

	serpent	tine 1M	silica-a	lumina	sulfated	zirconia	М	gO	silica-alu	mina+ MgO	sulfated z	irconia + MgO
product	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C
acetaldehyde	10.1	18.0	9.4	14.8	2.1	7.2	2.5	7.4	4.0	10.3	6.0	12.5
propenal	0.6	0.9	1.1	1.1	1.5	0.8	0.5	1.0	1.2	0.9	0.9	0.5
acetone	22.4	16.7	9.4	7.6	19.6	11.8	8.2	15.3	5.2	9.6	17.8	14.3
methylglyoxal	6.2	8.7	6.0	5.0	5.2	6.9	3.9	9.9	5.3	7.6	6.6	5.4
methyl vinyl ketone	1.3	1.0	1.6	1.5	0.9	2.0	1.5	1.8	1.4	2.7	1.3	1.2
со	7.1	11.8	5.8	8.1	2.5	8.4	1.4	6.2	3.2	7.9	5.6	12.1
CO <sub>2</sub>	1.7	1.6	1.3	1.2	1.4	2.3	0.6	1.1	0.8	1.5	2.9	8.4
ethylene	5.6	13.9	4.4	9.3	0.3	4.6	1.1	7.5	1.5	8.2	1.3	6.2
propene	0.6	1.0	1.1	2.8	0.3	1.7	0.2	0.8	0.6	1.8	0.4	0.8
unconverted acetol	0	0	16.2	0.9	24.3	3.6	44.7	11.1	12.9	0.7	5.1	0
coke <sup>b</sup>	-	21.7	-	29.8	-	31.0	-	18.2	-	34.2	-	33.2
carbon balance <sup>b</sup>	-	95.3	-	82.1	-	80.3	-	80.3	-	85.4	-	94.6

Table of Freduct distribution from catalytic conversion of accetor over anterent catalysis
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<sup>*a*</sup>All numbers are based on carbon yield. Reaction conditions: vaporization temperature = 300 °C; catalyst temperature = 445 °C or 500 °C; flow rate = 90 ml/min; reactant loading = 0.4  $\mu$ l; catalyst loading: 17 mg for serpentine 1M, 4.2 mg for silica-alumina, 9.0 mg for sulfated zirconia, 5.7 mg for MgO. <sup>*b*</sup>Coke was only measured for catalysis at 500 °C and carbon balance was only shown for catalysis at 500 °C.



**Figure 14.** Catalytic conversion of acetol over the different catalysts utilizing the same number of acid and/or basic sites; (a) 445 °C and (b) 500 °C. Reaction condition: same as Table 8; yield is the carbon yield; oxygen content in products is in wt%; products refer to deoxygenation products as shown in Figure 1, not including CO,  $CO_2$  and  $H_2O$ .

Methylglyoxal was formed by acetol dehydrogenation, likely in a similar fashion to 2,5furandicarboxaldehyde from HMF. The methylglyoxal selectivity was higher with MgO than silicaalumina and sulfated zirconia, suggesting MgO better promoted dehydrogenation. The hydrogen formed during dehydrogenation might have promoted acetol conversion to acetone in a similar manner as HMF conversion to 5-methyl furfural by cooperative catalysis between acidic and basic sites. This result was evident from the fact that the acetone selectivity with serpentine 1M was generally higher than with the individual acid or base catalysts. Acetaldehyde was formed by C-C cleavage either from acetol or methylglyoxal. Formation of acetaldehyde from acetol was accompanied by the formation of formaldehyde, which was identified in the mass spectrum. Methylglyoxal decarbonylation would also generate acetaldehyde, as evident by acetaldehyde and CO being the major products during methylglyoxal conversion (Table 9). As shown in Table S3, the selectivity towards acetaldehyde and CO increased with temperature as more fragmentation occurred at higher temperature. The selectivity for products formed by C-C cleavage, such as acetaldehyde, CO and ethylene, was higher with silica-alumina than MgO, which was similar to HMF conversion. Interestingly, sulfated zirconia, the stronger acid, did not promote C-C fragmentation as much as did silica-alumina perhaps do to coking of the stronger acid sites. Propenal and methyl vinyl ketone were probably formed by aldol condensation between formaldehyde/acetaldehyde and formaldehyde/acetone, as discussed previously.

As hydrogen was formed *in situ* during the reaction, the olefins might have been formed from acetaldehyde and acetone through a hydrodeoxygenation (HDO) mechanism. Several literature studies reported transition metal oxides, such as MoO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO and WO<sub>3</sub>, were active for the HDO process to convert acetaldehyde or acetone to ethylene or propylene, respectively.<sup>84-89</sup> From density functional theory (DFT),<sup>84,85</sup> it was postulated that the double bond on the carbonyl group was converted to a single bond by hydrogen transfer to the carbonyl carbon leading to easier bond cleavage as the C-O bond had a lower dissociation energy than the initial C=O bond. The oxygen from the C-O bond subsequently interacted with a metal site to form a metal-oxygen bond. The adsorbed reactant could lose one alpha H by interacting with a nearby O on the metal oxide to form a hydroxyl on the catalyst. Cleavage of the C-O bond then readily formed the olefin. A water molecule could be formed by recombination of the two hydroxyls on

the catalyst surface, accompanied by generation of an oxygen vacancy site. The metal oxides used in the current study might also promote the oxygen removal from the carbonyl group in a similar fashion as HDO. The hydrogen molecule formed by dehydrogenation or the hydrogen atom in a transition state during dehydrogenation could be transferred to the carbonyl carbon. The absence of alcohol formation in the current study inferred only one hydrogen atom was transferred to the carbonyl carbon instead of two, which would saturate the C=O bond. The low conversion found from directly feeding alcohol demonstrated the alcohol, if formed by hydrogen saturation of the C=O bond, would not readily dehydrate to olefins under these reaction conditions. Metal atoms in the acid/base catalyst, especially Mg that has a low electronegativity, might facilitate metal-O bond formation. The oxygen on the metal oxide might act as a basic site to abstract an alpha hydrogen in carbonyl compound. C-O fragmentation could then form the olefin.

In summary, the speculated reaction network is shown in Figure 15. The detection of hydrogen formation is shown in Figure S15. A basic site facilitated dehydrogenation of acetol to form methylglyoxal. An acid site could then promote C-C cleavage to form acetaldehyde and CO. The hydrogen formed during the dehydrogenation might participate in acetone formation from acetol by removing oxygen as water in a similar fashion to 5-methyl furfural formation from HMF. The hydrogen might also take part in acetaldehyde and acetone HDO to form ethylene and propene, respectively. The highest degree of deoxygenation achieved by the serpentine 1M catalyst was primarily attributed to the high conversion and selectivity towards olefins and acetone.



**Figure 15.** Speculated reaction network for catalytic deoxygenation of acetol over the acid/base catalyst.

**3.6. Reaction Pathways for Methylglyoxal Conversion.** Despite its equivalent oxygen content, lower methylglyoxal conversion was observed than with acetol as shown in Figure 16. Methylglyoxal has two less hydrogen atoms, so diminished intermediate hydrogen via dehydrogenation would be available. As noted in Figures 14 and 16, the depressed hydrogen availability would necessitate conversion of methylglyoxal primarily through decarbonylation. This reaction was evident by the high selectivity towards acetaldehyde and CO. Compared to acetol, much less olefins were observed from methylglyoxal conversion, which could also be due to less hydrogen being available for HDO. Similar to the catalytic conversion of HMF and acetol, silica-alumina gave higher decarbonylation activity compared to sulfated zirconia or MgO as shown by its higher selectivity towards CO and acetaldehyde (Table S4 in supporting information). Also, more C-C fragmentation occurred at higher reaction temperature, as evident by the acetaldehyde

and CO yields. In terms of deoxygenation performance, the highest conversion and lowest oxygen content in the products were observed with serpentine 1M at both temperatures, with a 30% decrease in oxygen content after conversion at 500 °C. The deoxygenation products yield was the second highest with serpentine 1M, only being less than that with silica-alumina.

	serpent	tine 1M	silica-a	lumina	sulfated	zirconia	M	gO	silica-alu	mina+ MgO	sulfated z	irconia + MgO
product	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C	445 °C	500 °C
acetaldehyde	10.5	11.7	14.9	15.9	3.8	5.0	7.3	9.5	12.8	13.6	6.6	6.7
propenal	0.9	0.8	0.7	1.1	0.4	0.4	0.5	0.8	1.0	0.7	0.7	0.7
acetone	0.9	1.4	0.7	0.9	1.2	1.4	1.0	0.9	1.2	1.0	0.7	1.0
methyl vinyl ketone	0.3	0.4	0.1	0.2	0.3	0.3	0.3	0.1	0.4	0.4	0.6	0.5
СО	4.1	7.1	5.9	7.4	2.1	4.0	3.4	3.5	5.2	5.8	3.7	7.0
CO <sub>2</sub>	1.3	2.0	0.9	1.1	1.3	3.6	1.2	1.4	1.5	1.8	2.6	4.6
ethylene	0.8	1.4	0.6	0.7	0.0	0.0	0.2	0.5	0.5	0.2	0.0	0.7
propene	0.2	1.0	0.9	1.3	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.1
unconverted methylglyoxal	54.1	51.3	55.0	57.4	71.3	67.2	66.5	65.8	59.1	61.9	69.3	63.0
coke <sup>b</sup>	-	19.5	-	4.5	-	9.5	-	8.9	-	9.4	-	11.3
carbon balance <sup><math>b</math></sup>	-	96.6	-	90.5	-	91.5	-	91.7	-	94.7	-	95.6

# Table 9. Product yield from catalysis of methylglyoxal over different catalysts<sup>a</sup>

<sup>*a*</sup>All numbers are based on carbon yield. Reaction conditions: vaporization temperature = 300 °C; catalysis temperature = 445 °C or 500 °C; flow rate = 90 ml/min; reactant loading =0.4  $\mu$ l; catalyst loading: 17 mg for serpentine 1M, 4.2 mg for silica-alumina, 9.0 mg for sulfated zirconia, 5.7 mg for MgO. <sup>*b*</sup>Coke was only measured for catalysis at 500 °C and carbon balance was only shown for catalysis at 500 °C.



**Figure 16.** Catalytic conversion of methylglyoxal over the different catalysts using the same number of acid and/or basic sites; (a) 445 °C and (b) 500 °C. Reaction condition: same as Table 9; yield is the carbon yield; oxygen content in products is in wt%; products here refer to deoxygenation products as shown in Figure 1, not including CO,  $CO_2$  and  $H_2O$ .

**3.7. Stability Test.** The stability of serpentine 1M was tested using multiple injections of HMF. The reaction results after each injection are shown in Figure 17. No significant loss of activity was observed up to 10 injections as evidenced by steady conversions and total yield of products.



**Figure 17.** Stability of serpentine 1M for catalytic conversion of HMF. Reaction conditions: vaporization temperature = 300 °C; catalyst temperature = 500 °C; flow rate = 90 ml/min; reactant loading is 0.4 mg for each injection; catalyst loading: 17 mg.

**3.8. Further Discussion and Summation.**  $CO_2$  was formed during the catalytic conversion of HMF, acetol and methylglyoxal. Since none of these three reactants nor their products contained a carboxylate group, the formation of  $CO_2$  should not be due to decarboxylation. Instead, its formation was likely through the water-gas shift reaction with CO and H<sub>2</sub>O, which is known to occur at the these reaction temperatures with metal oxide catalysts.<sup>90,91</sup>

The conversion of HMF, acetol and methylglyoxal over the different acid/base catalysts suggested that the acidic sites better promoted fragmentation/decarbonylation while the basic sites promoted dehydrogenation. Oxygen removal via the hydroxyl group was facilitated by cooperation between the acidic and basic sites. Serpentine 1M, which had closely located acid and base sites, was most active for the catalytic deoxygenation of oxygenates due to their synergy. The physical mixture of acid and base catalysts did not achieve the same deoxygenation performance as the serpentine 1M, possibly due to the relative isolation of the acid and base sites, which impeded their cooperativity.

To summarize the model compound results, an acid-base bifunctional catalyst facilitated oxygen removal. Oxygen rich compounds were generally more reactive since a greater number of oxygen functional groups enhanced the probability of interaction with the catalytic active sites either by hydrogen transfer or the formation of a metal-oxygen bond. Initially, these oxygenates underwent a series of reactions, including dehydrogenation, decarbonylation and dehydration, to form products with fewer oxygen atoms. These first-stage products could further react through two types of reactions. One was aldol condensation of the compounds with a carbonyl group, which generated an aldehyde or ketone with a longer chain length. The other was HDO of the small aldehydes or ketones using *in situ* generated hydrogen. As a result, less oxygenated, more stable, and longer chain molecules could be formed as partially deoxygenated products while olefins could be formed as completely deoxygenated products. The oxygen functional groups in these bio-oil model compounds were representative of those found in real bio-oil derived from carbohydrate pyrolysis, so the use of an acid-base bifunctional catalyst for *in situ* or *ex situ* catalytic pyrolysis of carbohydrates would be interesting.

#### 4. CONCLUSION

Catalytic deoxygenation of eight carbohydrate-derived bio-oil model compounds was performed in a fixed bed reactor. Aldol condensation was tested separately by feeding binary mixtures of the model compounds. Using the same number of acid/base sites, an acid, base, a physical mixture of acid and base, and an acid-base bifunctional catalyst were evaluated based on their activity for deoxygenation reactions. The bifunctional catalyst was prepared by acid treatment of a natural mineral, serpentine. Extensive characterization of the bifunctional catalyst revealed adjacent acidic and basic sites. Compared with the physical mixture the bifunctional catalyst had higher activity for aldol condensation. During catalytic conversion of single model compounds, a higher reactivity was observed for the compounds with greater amount of oxygen-containing functional groups. Based on isotopic labelling, reaction pathways were proposed for the catalytic conversion of three oxygen rich compounds, HMF, acetol and methylglyoxal. A series of deoxygenation reactions occurred, including decarbonylation, dehydration, and aldol condensation. A moderate acid strength better promoted decarbonylation. In situ hydrogen was likely formed during the catalysis as evident by the presence of dehydrogenation products, which appeared promoted by basic sites. The *in situ* hydrogen probably participated in the hydrodeoxygenation of small aldehyde/ketones to completely remove oxygen since olefins were observed in the products. By evaluating the yield of deoxygenation products and oxygen content in the product mixture, the highest degree of deoxygenation was achieved with a bifunctional catalyst, due to the synergistic catalysis between acid and base sites, which was not seen with the physical mixture of acids and bases. Additionally, the bifunctional catalyst maintained stability through a number of catalytic cycles. The current study suggested that acid treated serpentine or potentially another cost-effective acid-base bifunctional catalyst, could be possible candidates for efficient oxygen removal in the catalytic pyrolysis of carbohydrates.

# ASSOCIATED CONTENT

# **Supporting Information**

Experimental details, additional characterization results (nitrogen physisorption, TPD-MS, SEM images, EDS maps, XRD patterns), characterization of synthesized HMF, details for isotopic tracking, selectivity of products, catalytic conversion of 5-methyl furfural and furfural, detection of hydrogen during catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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