Mechanistic Insights into the Production of Methyl Lactate by Catalytic Conversion of Carbohydrates on Mesoporous Zr-SBA-15

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Abstract

The as-synthesized Zr-SBA-15 catalysts with tunable mesoporous structures showed excellent catalytic performance for the conversion of carbohydrates to methyl lactate in a “one-pot” process using near-critical methanol or methanol-water mixture as the solvents. The effects of reaction conditions, including temperature, reaction time, and catalyst loading amount, on the conversions of carbohydrates and the yields of methyl lactate were investigated. The high yields of methyl lactate, up to 41 % and 44%, were produced from pentose and hexose, respectively, in the near-critical methanol at 240°C. Moreover, the Si/Zr ratio of the Zr-SBA-15 catalysts profoundly affected the Lewis acidity and therefore the catalytic activity and selectivity to methyl lactate in the conversion of carbohydrates. The pore size of the Zr-SBA-15 catalysts, tuned by the synthesis temperature, strongly affected the formation of solid residues. The key intermediates such as glyceraldehyde, glycolaldehyde, and pyruvaldehyde were used as probe reactants to understand the mechanism. The role of the Zr-SBA-15 catalyst in the aldol- and retro-aldol condensation, isomerization, and Cannizzaro reactions of carbohydrates and their derivatives was discussed. Furthermore, 28% and 27% yields of methyl lactate were obtained from cellulose and starch, respectively, in methanol-water mixture (5 wt% water and 95 wt% methanol) at 240°C. The Zr-SBA-15 catalyst was relatively stable in short term without regeneration.

Keywords: Methyl lactate; Carbohydrate biomass; Mesoporous silica; Zr-SBA-15; Lewis acid

1. Introduction

The development of efficient methods to make fuels and chemicals from lignocellulosic biomass is vital to reduce the dependence on fossil fuel feedstocks [1–3]. The production of value-added chemicals from carbohydrates using non-toxic heterogeneous catalysts is an appealing environmentally benign process. Various endeavors have been made over the past few years to develop stable, recyclable solid catalysts for the conversion of biomass by catalytic methods[4–7]. Microporous zeolites are efficient catalysts in the transformation of small molecules; however, they become unsuitable when the essential reactants involved in the catalytic process are sized comparably with the zeolite pore dimensions. The rational approach to overcoming mass-transfer limitations would be to increase the diameter of the pores, thus bringing them into the mesoporous range with a key factor here being the shape selectivity properties of these catalysts [8–13]. Shape selectivity enables excellent adjustment of catalytic transformation exclusivity, and also acts on the activity and stability of the catalyst by either protecting the acid sites from potential contaminants (in particular, coke precursors) which are contained in the feeds, or by inhibiting the formation of coke precursors in the pores. However, few reports exist on biomass conversion with mesoporous silicate materials. This scarcity of literature is due to the fact that a pure mesoporous silica material possesses a neutral framework, as well as its propensity to exhibit inherently negative traits such as poor hydrothermal stability and low catalytic activity, which limit its application as a catalyst medium [14,15]. In order to enable their application in catalysis, different structured mesoporous silicate materials have been investigated and various metal ions have been incorporated into the host mesoporous silica materials [16–20]. In particular, the isomorphic substitution of silicon with transition metals has

proven to be an excellent strategy to generate catalytically active sites in mesoporous silicate materials [14,21–23].

Among the mesoporous materials, the SBA-15 of 2D hexagonal-ordered structure with tunable pores in 4-10 nm has received much attention in the past decades due to its relatively large pore size and high hydrothermal stability in comparison with other mesoporous silica materials, such as MCM-41, its analog in M41S family [24]. This large pore channel network provides a distinctive open space, with easy and direct access for both guest and host species, thus facilitating inclusion and/or diffusion throughout the pore channels without pore blockage. Such properties spur the prospective utilization as catalysts and adsorbents [21,25,26]. On the other hand, zirconia-based materials have been widely applied in catalyzing various types of reactions such as oxidation, dehydration, hydrogenation, and hydroxylation [27–30]. Mesoporous silicate materials containing zirconium have high special surface areas and potential Lewis acid properties [14,31]. The basic structural unit of mesoporous silicate frameworks consists of a silicon atom that is coordinated to four oxygen atoms. Zirconium atoms have a coordination number of 7 or 8 in zirconia materials. When replacing Si^{4+} with Zr^{4+} , a zirconium atom has only 4 coordinated oxygen atoms, resulting in empty zirconium d-orbitals which can act as electron acceptors, i.e. Lewis acid sites [32].

Carbohydrates constitute the largest portion of lignocellulosic biomass, and various strategies for their efficient use as a commercial chemical feedstock as a petroleum supplement are being established to synthesize value-added chemicals. The synthesis of lactate acid esters in related alcohols with renewable carbohydrate biomass as the feedstock invokes lots of interests in that lactate acid esters are “green” solvents which have numerous applications in the chemical, food, pharmaceutical, and cosmetic industries [33–37]. Various strategies to produce lactic acid

esters have been established including both fermentative processes [38] and catalytic transformations [39,40]. Catalytic methods have many advantages over that involving fermentation method especially considering the latter approach's unavoidable large amounts of salts by-products, which impose a high environmental remediation cost. Studies on the conversion of carbohydrates to lactate esters over heterogeneous catalysts have emerged recently. For instance, Holm *et al.* [41,42] reported that Lewis acidic zeotype materials, such as Sn-Beta, catalyzed the conversion of mono- and disaccharides to methyl lactate (ML) in methanol at 160°C with a 16-hour reaction time. With sucrose as the substrate, the ML yield reached a record high of 68%, while when the alkali ion of K_2CO_3 was added to the solvent mixture, the ML yield was further promoted to 75% at 170 °C [43]. Carlos reported that with the Sn-MCM-41 which has an atomic ratio of Si/Sn=55, a 43% yield of ML was produced from the conversion of glucose after 20 hours at 160°C [44]. The carbon-silica composite grafted Sn(IV) showed well-balanced Lewis/Brønsted acidity and yielded 45% ML from the conversion of sucrose in methanol[45]. Sn-MWW zeolite was also demonstrated to be an effective and selective catalyst for the direct conversion of mono-and disaccharides to ML[46]. However, the main drawbacks of tin-based materials are the typically complex and lengthy synthesis process and the toxicity of tin precursors, which may hamper their industrial applications[47]. Solid base catalysts, including hydrotalcites [48] and magnesium oxide [49], and supported noble metal catalysts [39] were also used for catalyzing the formation of lactic acid or ML from glucose at rather low yields.

Recently, alcohols have been utilized as an alternative solvent in the liquefaction of various types of biomass, including cellulose, lignin, sewage sludge, and microalgae, due to their advantages with better solubility of organic intermediates, hydrogen donor properties, and easier

separation due to their low boiling points [50–59]. Compared to water, alcohols such as methanol and ethanol have much lower critical temperatures and pressures. Thus at relatively mild conditions, near- critical and supercritical alcohols can act not only as a solvent but also as a reactant, which can serve as a hydrogen donor agent to remove oxygen from biomass and a radical quenching agent to retard repolymerization and formation of humins [60–63]. Methanol, a small and highly polar molecule, still exhibits weak hydrogen bonding even at the critical temperature ($T_c = 239.4^\circ\text{C}$) [64,65], which facilitates the methanolysis of large biomass molecules.

Herein we report our findings on the catalytic conversion of carbohydrates to methyl lactate using a mesoporous Zr-SBA-15 catalyst in near- critical methanol solvents ($T \leq 240^\circ\text{C}$), which combines the lactic acid production and esterification into a “one-pot” reaction system. A possible reaction mechanism and structure-activity relationship are proposed to explain the performance of the Zr-SBA-15 as a heterogeneous Lewis acid catalyst in the production of ML from various carbohydrates including pentose, hexose, starch and cellulose.

2. Experimental Section

2.1 Materials

The following reagents and products were used as received without further purification. D-(+)-xylose (99%), D-(+)-glyceraldehyde (98%), Fructose (99%), Sucrose (99%), glycolaldehyde dimer, pyruvaldehyde (40wt% solution in water), furfural (99%), 5-(hydroxymethyl) furfural (99%), hydrochloric acid (36.5-38.0%, BioReagent), triblock copolymer Pluronic P123, tetraethyl orthosilicate (>99.0%), n-butanol (>99.0%) and zirconyl chloride octahydrate (98%) were purchased from Sigma Aldrich. D(+)-Glucose (Reagent ACS Grade) were purchased from Acros Organics. Methyl lactate (97%), erythrose syrup (70% w/v),

methyl levulinate (99%), methyl glycolate (98%) and glycolaldehyde dimethylacetal (98%) were purchased from Alfa Aesar. Microcrystalline cellulose (average particle size 50 μm) and cellobiose (98%) were purchased from Acros Organics. Starch (powder, certified ACS, soluble) and sucrose (crystalline, certified ACS) were purchased from Fisher Scientific. Galactose, mannose, and arabinose were purchased from Carbosynth.

2.2 Catalyst preparation

The Zr-SBA-15 materials were synthesized following the procedure described by reference [24]. Briefly, 2 g of Pluronic P123 was added to 75 ml of 1.6 M HCl solution. The mixture was stirred at 40 °C for 3 hours until all P123 was dissolved. Next, 4.25 g of TEOS and an appropriate amount of zirconyl chloride octahydrate were added into the solution and the mixture was stirred for another 24 hours at 40°C. The resulting gel was placed in the Teflon-lined autoclave and heated at a range of temperatures of 80-150 °C for 24 hours. The solid product was filtered with mild washing, dried at 100 °C overnight, and calcined in flowing air at 550 °C for 6 hours. The x (in Zr-SBA-15-x-y°C) represents the mole ratio of Si/Zr, the y represents the hydrothermal temperature. Zr-SBA-15-y°C without x means that the mole ratio of Si/Zr is 20. Zr-SBA-15-x without y means that the catalyst was synthesized at 100°C. Zr-SBA-15 without x and y means that the catalyst was synthesized at 100°C with Si/Zr=20.

2.3 Catalyst characterization:

Small-angle X-ray Scattering (SAXS) was performed using a sample-to-detector distance of 172.1 cm, which provided a two-theta range of approximately 0.3-2.0 degrees. Data was typically collected over 30 seconds at a temperature of 20°C. The X-ray source was Cu K α radiation with a wavelength of 1.54 Å, which was generated by a Rigaku Ru-200BVH rotating

anode. Measurements were made on a Siemens HI-STAR multi-wire area detector and were corrected for background and non-linearities in the detector. Integration of the 2D measurement provided a 1D plot of intensity (arbitrary units) versus the two-theta scattering angle, which was peak-fitted using Material Data Incorporated's JADE.

Transmission electron microscope (TEM) micrographs were captured using JEOL-JEM 2100F operating at 200 kV. The samples were dispersed in 1-butanol, and a drop of the suspension was placed on lacey carbon supported on 300 mesh copper grids.

N₂ physisorption isotherms were measured on an Autosorb-iQ system (Quantachrome) at 77 K. Outgassing was done at 523 K until pressure rise in the test cell was less than 25 mTorr/min. Pore size distribution and cumulative adsorbed volume were calculated by using NLDFT (nonlocal density functional theory) adsorption model which describes N₂ adsorbed onto silica at 77 K in cylindrical pores (AsiQwin 1.02, Quantachrome). NLDFT model considers the configuration of adsorbates in pores on a molecular level and is widely used to characterize ordered porous materials with different pore geometries. With adequate fluid–fluid and fluid–solid interaction parameters, it has been used to quantitatively predict the capillary condensation and evaporation transitions of adsorbates in mesoporous materials.

In a typical NH₃ temperature programmed desorption (TPD) experiment using a Micromeritics AutoChem 2920 Chemisorption Analyzer, the catalyst was first degassed in helium at 250°C for 1 hour, then the temperature was cooled till 100°C in helium flow. After that, 10% ammonia in helium was adsorbed on the catalyst at 100°C for 60 min and then the helium flow at 50 mL/min was used to remove physically adsorbed ammonia. Finally, the NH₃ TPD was carried out from 100°C to 550°C with a temperature ramp of 10°C /min.

Drift-IR study was performed on EQUINOX 55 (Bruker) equipped with a MCT

detector. The samples were degassed at 550 °C for 1 hour under helium in a high temperature reaction chamber containing a Praying Mantis TM diffuse reflection attachment (Harrick). Small aliquots of pyridine were carried by helium and exposed to the sample at room temperature for 15 minutes. Prior to the characterization, the physically adsorbed pyridine was removed by flowing helium at 250°C under helium for 1 hour. All spectra were collected at 120°C.

2.4 Catalytic reactions

Reactions were carried out in a 100 mL stirred Parr micro reactor, whereby the catalyst was suspended in a solution of biomass substrate in methanol (20 ml) and the reactor was charged with 400 Psi N₂ initially and then heated at a ramp rate of 10 °C/min until the desired set temperature was reached. During the reaction, mixing was achieved through an internal propeller operating at 700 RPM. Once the set temperature was attained, the reactor was held for the set reaction time, and then quenched quickly in an ice bath to stop the reaction. The reactor was cooled to approximately 25°C before being vented after the gas pressure was recorded. The reactor was then immediately broken down and the solid residue remaining in the reactor was recovered and dried. The aqueous and solid fractions were separated using a centrifuge.

2.5 Product analysis

After the reaction, the resultant liquid phase product samples were prepared for analysis with a gas chromatography coupling with flame ionization detector (GC-FID), a high performance liquid chromatography (HPLC) and a gas chromatography coupling with mass spectrometer (GC-MS).

The liquid products (e.g. furfural, HMF) were quantified by HPLC analysis using a Shimadzu HPLC system equipped a UV-VIS Detector (Shimadzu SPD 10-AV) and Refractive Index Detector (Shimadzu RID-6A). The liquid phase after reaction was filtered through a 0.45

micron syringe filter, and then diluted 10 times with DI water. The samples were separated in an Aminex 87-H column from Bio-Rad, using 5 mM H₂SO₄ as the mobile phase (0.7 mL/min flow rate) at a column temperature of 55°C. The UV-VIS detector was utilized at 208 nm and 290 nm.

The liquid products identified in the methanol were qualified and quantified by GC-MS and GC-FID analysis, respectively. The liquid phase after reaction was filtered through a 0.45 micron syringe filter before being diluted 10 times with methanol. The sample were injected in an Agilent 6890 series GC-MS equipped with an Agilent DB5-MS column (30 m x 0.25 mm ID, 0.25 μ m film thickness) and an Agilent 5973 Mass Selective Detector. The same prepared sample were also injected in a Shimadzu GC-2010 equipped with an SHRXI-5MS column (30m x 0.25 mm ID, 0.25 μ m film thickness) and an FID detector.

A Euro EA3000 CHNS-O analyzer (Eurovector) was used for measuring the carbon content in the solid residue samples.

3. Results and discussion

[Fig. 1](#) shows the yields of the main products using xylose as the feedstock with and without adding catalysts. A relatively low yield of ML (~8%) was produced at 240°C without adding a catalyst. With only the pure SBA-15, the ML yield was ~7.0%, which is close to that without catalyst. Both the as-synthesized Zr-SBA-15 and the commercial ZrO₂ resulted in noticeably higher yields of ML at 240°C for 1 hour. The 35.9% yield of ML was achieved with the Zr-SBA-15 catalyst, which was more than twice of the 16.4% yield with the ZrO₂ catalyst. To validate the catalytic effect of Zr ion in SBA-15, Ti ions were deliberately incorporated into the SBA-15 framework so as to compare with the Zr-SBA-15 catalyst. It was found that with the Ti-SBA-15 catalyst, the yield of ML from xylose was comparable to that with the ZrO₂ catalyst but was still much lower than that with the Zr-SBA-15 catalyst. Notably, without a catalyst or

with the Ti-SBA-15 catalyst, there were negligible amount of furfural yields, 0.7% and 0.8%, respectively. In contrast, when SBA-15, ZrO₂ and Zr-SBA-15 were employed, the furfural yields reached to 5.1%, 6.4% and 7.9%, respectively. The mesoporous structure of the silica framework with the presence of zirconium ions confers strong Lewis acidity as well as weak Brønsted acidity.[66] It is well accepted that Lewis acid catalysis can facilitate the retro-aldol condensation of a sugar molecule, which is the initial step in the conversion of sugars to lactic acid [41], while a Brønsted acid catalyzes the dehydration of xylose to form furfural. The co-production of ML and furfural from xylose with the Zr-SBA-15 catalyst suggest that both the Lewis and Brønsted acidic properties co-existed on the catalyst surface.

To further examine the catalytic effect of zirconium loading of the Zr-SBA-15 catalyst, the catalysts with different Si/Zr molar ratios of 100, 60, 40, 20 and 10 were prepared. As shown in Fig. 2, the total acid strength analysed by the NH₃ TPD increased with increasing the zirconium loading on the SBA-15 silicate. Fig. 3 shows the yields of the three major products, ML, glycolaldehyde dimethyl acetal (GADMA), and furfural, on the Zr-SBA-15 catalysts with various Si/Zr molar ratios under otherwise identical reaction conditions. Initially, with increasing the Zr loading, the yields of increased steadily. However, as the zirconia loading further increased till the Si/Zr mole ratio of 10, the yields of all three products decreased implying the abrupt change of the catalyst properties. The maximum yield of ML was found to be in the range of the Si/Zr mole ratios of 40 to 20, e.g., with the Zr-SBA-15-40 or Zr-SBA-15-20 catalyst, approximately 19% ML and 11% GADMA were produced at 180°C. However over-loading of Zr ions onto SBA-15 inhibited the catalyst's performance. Therefore, to confirm the structures of the Zr-SBA-15 silicate materials at different Si/Zr ratios, the small-angle X-ray scattering (SAXS) characterization was performed. As depicted in Fig. 4, the SAXS spectra

exhibited the strong (1 0 0), (1 1 0) and (2 0 0) diffraction peaks at 2θ angles between 0.5° and 2° for the samples with the Si/Zr ratios from 100 to 20, which indicated the structural ordering with the symmetry of the 2D-hexagonal space group $p6mm$ [9,14,31]. However, a further increase in Zr loading (Si/Zr = 10) drastically lowered the peak intensity suggesting that incorporating too many Zr heteroatoms was detrimental on the structure of the mesoporous SBA-15 framework, which was coincident with its low catalytic performance. From the high-resolution TEM images (Fig. S1), highly ordered pore structure was evident for the Zr-SBA-15 materials at the Si/Zr mole ratio of 20, while the ordered mesoporous structure was destroyed when the Si/Zr mole ratio reached 10, which were consistent with the SAXS data.

To maximize ML yield, process conditions were optimized for the xylose conversion reactions. As shown in Fig. 5, the varying temperature has a pronounced effect on the production of ML, yielding a steadily increasing amount of ML up to 35.9% with an increase in temperature from 160°C to 240°C for a 1-hour reaction. The yields of other products such as furfural also increased steadily with increasing temperature. The yield of GADMA, however, decreased from 10.9% at 180°C to 1.6% at 240°C . The highest ML yield of 40.8% was achieved when the reaction time extended to 6 hours at 240°C as shown in Fig. 6. However, the ML yield varied little as the reaction time was longer than 3 hours. Conversely, the yields of GADMA and furfural consistently decreased with extending the reaction time. Of particular interest is the fact that GADMA almost completely vanished after 3 hours at 240°C . These results suggested that longer reaction time leads to the decomposition of GADMA and furfural. It is also interesting to find that the methyl levulinate yield increased with reaction time at 240°C . The effects of different catalyst loading amounts on the conversion of xylose were also examined. As depicted in Fig. 7, the yields of both ML and furfural showed a similar uptrend with constantly increasing

catalyst loading, while those of GADMA and methyl glycolate decreased steadily. However, as the mass ratio of catalyst to xylose was larger than 0.2, the yield of ML was almost unchanged and reached to a plateau. By substituting methanol with water as the solvent (Table 3 entry 4), the lactic acid yield was ~5.9% while the furfural yield was ~42.3% with Zr-SBA-15. In contrast, the yields of furfural and lactic acid were only 21.2% and 3.0%, respectively, without adding any catalyst. Thus the Lewis acid property of the Zr-SBA-15 catalyst appeared to vanish and be transformed to Bronsted acid in water.

For chemical reactions in confined channel space in mesoporous silicate materials, interesting pore size effects can be expected.[67–69] The pore size of the Zr-SBA-15 catalyst can be tuned by optimizing the hydrothermal treatment conditions during the synthesis.[70] [Fig.8](#) shows the pore size distribution determined by NLDFT model for the Zr-SBA-15 materials with different synthesis temperatures. The pore sizes of Zr-SBA-15-80°C, Zr-SBA-15-100°C, Zr-SBA-15-120°C and Zr-SBA-15-150°C, were 7.6, 9.1, 9.8 and 10.6 nm, respectively. With increasing the hydrothermal temperature, the pore diameter of the SBA-15 materials increased while the BET surface area decreased. The ML yield varied slightly with increasing the pore size except the catalyst synthesized at 80°C in the smallest pore size, as shown in [Table 1](#). In contrast, the furfural yield and the corresponding solid residue yield decreased significantly with increasing the pore size. It is well known that aldehyde compounds such as furfural are prone to polymerize and form humins at elevated temperatures. Apparently, large pores in a Zr-SBA-15 catalyst provides more open pore space where guest and host species can easily access, thus facilitating the diffusion in and out the stoma channels without pore restriction. It turns out that in order to minimize the undesirable by-products such as furfural and humins, it is important to lift the pore diffusion limit of the Zr-SBA-15 catalyst for this particular ML production reaction.

Recyclability and reusability are of importance for the heterogeneous Zr-SBA-15 catalysts. During the typical reaction, the yield of solid residue on the catalyst was relatively low, ~10.8%. However, the activity of the catalyst could decrease if solid residue continues to build up on the catalyst surface in the subsequent repeating reactions. Fig.9 shows that the yield of ML from xylose only decreased slightly over five consecutive runs with the re-used catalyst without regeneration, suggesting that the Zr-SBA-15 catalyst was relatively stable, although a regeneration process to remove the solid residues would be desirable for the catalyst re-use. It is very interesting to find that the yield of solid residue (10.7%) on the catalyst after the 5th run almost did not change compared with that after the first run (10.8%), implying that the formation of extra coke inside the pores was inhibited after the catalyst was used once. The high-resolution TEM images of the Zr-SBA-15 samples before and after reaction showed that the highly ordered pore structure maintained without any noticeable pore size shrinkage or blockage, as shown in Fig. 10. Furthermore, ML was used as reactant to test its stability. It was found that only 3% of ML was decomposed after a one-hour reaction at 240°C with the Zr-SBA-15 catalyst in methanol (Fig. S2), thus indicating that ML, the final product of xylose conversion, was very stable in this reaction system.

It is well accepted that Lewis acids can promote retro-aldol condensation as the initial step in the conversion of sugars to lactic acid [41]. We thus propose that the reaction pathway of converting xylose to ML over the Zr-SBA-15 catalyst begins at the retro-aldol condensation forming glycolaldehyde and glyceraldehyde, as shown in Scheme 1. Fig. S3 illustrates the total acidity of the Zr-SBA-15 samples calculated from the NH₃ TPD. The pure SBA-15 silicate did not show any appreciable ammonia adsorption (only 0.02 mmol NH₃/g), while the Zr-SBA-15 samples presented high acidity of ~0.7 mmol NH₃/g. In our previous study, it was confirmed by

the pyridine-FTIR that the Lewis acid sites were dominant on the Zr-SBA-15 catalyst. The Zr^{4+} ions in the SBA-15 silica framework as the Lewis acid sites first interacted with the carbonyl group of xylose, and then broke the C5 xylose molecule down to C3 glyceraldehyde and C2 glycolaldehyde. Glyceraldehyde underwent dehydration to form 2-hydroxypropenal, then to pyruvaldehyde via keto-enol tautomerization, and finally to ML in methanol solvent by possible intramolecular Cannizzaro and esterification reactions. Although trioses were able to be converted to ML via Meerwein-Ponndorf-Verley reduction with methanol[71], the direct evidence of converting pyruvaldehyde to ML through intramolecular Cannizzaro reaction was that no deuterium was incorporated into the hydrocarbon backbone of ML in the isotopic CD_3OD solvent [72]. On the other hand, the by-product, GADMA, was formed by the acetalization of glycolaldehyde with methanol.

To validate our hypothesis of the reaction pathway, the possible key intermediates, glyceraldehyde, dihydroxyacetone, pyruvaldehyde, glycolaldehyde, and GADMA were used as the probe reactants. It was found that much higher ML yields (78.8% and 84.5%) were obtained from glyceraldehyde and dihydroxyacetone, respectively (Table 3 Entries 6 and 8), than from xylose. The yield of ML was even close to 100% from pyruvaldehyde (Table 3 Entry 10). Yet in the absence of the Zr-SBA-15, much lower amounts of ML were produced from all three probe reactants. More interestingly, using glycolaldehyde as the probe, a high amount of GADMA was produced without catalyst, while ~ 61.3% ML was obtained with the Zr-SBA-15 catalyst. It appeared that C–C bond forming aldol condensation reactions occurred in the presence of Zr-SBA-15 in that the C4 acid ester products, e.g., methyl vinylglycolate and methyl 2-hydroxybutanoate, were also observed as the products from the C2 reactant, glycolaldehyde (Fig. S4). Very interestingly, when using GADMA as the probe reactant, it was converted to ML in a

24% yield with the Zr-SBA-15 catalyst and the product distribution was similar to that using glycolaldehyde as the reactant: methoxyacetaldehyde dimethylacetal was another major product obtained through etherification while other products in the much lower yields were methyl vinylglycolate and methyl 2-hydroxybutanoate, as shown in [Fig. S5](#). It revealed that GADMA and glycolaldehyde were reversibly converted to each other and the aldol-condensation reactions occurred in the presence of Zr-SBA-15 to form C4 and C6 aldehydes, while the formation of ML suggested that retro-aldol condensation reactions took place subsequently. However, it is unclear how the etherification and esterification reactions with methanol evolved in parallel to the aldol condensation and retro- aldol condensation reactions. Since most glycolaldehyde intermediates could be further converted to ML with the Zr-SBA-15 catalyst in near critical methanol, the yields of ML from pentoses (xylose, arabinose) and hexoses (glucose, mannose) had no distinct difference, unlike the results of converting sugars to ML at 160-170°C using the Sn-Beta catalyst reported by Taarning and co-workers [42].

Furfural was the undesirable by-product from the dehydration of xylose, usually catalyzed by Brønsted acid. The furfural yield decreased sharply at high temperatures or for a long reaction time, while methyl levulinate yield increased at the same time during the xylose conversion with the Zr-SBA-15 catalyst. Using furfural as the probe reactant, the main product was methyl levulinate in the yields of 3.6% and 33.2% after reactions for 1 hour and 10 hours, respectively, at 240°C, as shown in [Fig. S6](#). Alkyl levulinate is known to be produced from furfuryl alcohol with solid acid catalyst [73]. A hydrogenation step is needed in the conversion of furfural to methyl levulinate, while methanol was the only hydrogen source in the probe reaction. We thus contemplate that furfural was converted into furfuryl alcohol via Meerwein-Ponndorf-Verley (MPV) transfer hydrogenation with methanol as the hydrogen donor, which

was probably promoted by the Lewis acid, followed by the conversion of furfuryl alcohol into methyl levulinate through ring-opening reactions with the aid of the weak Brønsted acid sites on the Zr-SBA-15 catalyst. Corma's group demonstrated the intermolecular transfer hydrogenation between alcohols and ketones in organic solvents using Sn-Beta and Zr-Beta as the solid Lewis acid catalysts [74–76].

The proposed reaction pathway for the conversion of xylose to ML can be generalized for the conversion of other cellulosic biomass. The retro-aldol condensation of pentoses and hexoses, however, may form different aldehyde or ketone products with solid Lewis acid catalysts [41,42]. The conversion of pentoses to ML can be divided as the following steps: retro-aldol condensation of an aldopentose leads to glyceraldehyde and glycolaldehyde, while retro-aldol condensation of a ketopentose forms dihydroxyacetone and glycolaldehyde. The outcome of both reaction pathways is the formation of a triose and a glycolaldehyde [42]. In contrast, the fragments formed from a hexose depend on the ketose or aldose form. Disintegration of an aldohexose leads to the fragments of a C4 aldotetrose and a C2 glycolaldehyde, while the ketohexose fragmentation results in two C3 fragments, dihydroxyacetone and glyceraldehyde [41]. With a Lewis acid catalyst, however, glucose and fructose can be inter-converted through isomerization before experiencing subsequent reactions [44,77]. [Table 3](#) shows that the disparate yields of ML were produced from glucose and fructose, respectively, while the comparable yields are seen for fructose and sucrose, the dimer of glucose and fructose (products were identified by GC/MS as shown in [Fig. S7](#)). Glucose yielded a lower amount of ML relative to fructose (37.3% versus 44.1%). The difference in the ML yields from different monosaccharides reflects the dynamic equilibrium between the isomerization, retro-aldol condensation and degradation reactions. In all cases, the conversions of both monosaccharides and disaccharides

were greater than 99% after 6 hours of reaction at 240 °C and the considerable yields of ML were formed using the Zr-SBA-15 catalyst (Table 3). Using disaccharides or polysaccharide including cellobiose, starch and cellulose as the reactants, substantially lower conversions were observed (products were identified by GC/MS as shown in Fig. S8). Cellobiose and starch, which are soluble in methanol, reached the similar yields of ML, 24.3% and 24.1%, respectively. However, only 16.7% ML was produced from cellulose at 240°C for a 10 hours reaction, suggesting that depolymerization is the bottleneck for cellulose conversion. In order to enhance the yield of ML from cellulose, a small amount of water (5 wt%) was added into methanol to facilitate the hydrolysis of cellulose. As the result, as high as 28.1% yield of ML was obtained directly from cellulose.

4. Conclusion

In summary, we demonstrate that methyl lactate was yielded from various carbohydrates in methanol solutions at near critical conditions with the Zr-SBA-15 catalysts. Under the optimum reaction conditions, the highest methyl lactate yields were 42% and 44% from pentoses and hexoses, respectively. The Zr-SBA-15 catalyst was relatively stable to produce methyl lactate from xylose after five consecutive catalytic reaction cycles without regeneration. The Lewis acid sites on the Zr-SBA-15 facilitated the retro-aldol condensation of carbohydrates, which was the initial step of the conversion of carbohydrates to methyl lactate. Increasing zirconium loading on the SBA-15 silica framework increased the total acid strength of the Zr-SBA-15 catalyst. However, over-load of zirconium could destroy the mesoporous structure of the SBA-15 silica. The large-pore Zr-SBA-15 catalysts inhibited the yields of undesirable by-products such as humins and furfural. Through the probe reaction studies, we conclude that C3 aldehydes/ketones including glyceraldehyde, dihydroxyketone, and perualdehyde were the key

intermediates to form methyl lactate from a variety of carbohydrate biomass. Zr-SBA-15 also catalyzed aldol condensation of C2 aldehydes to form C4 and C6 sugars, followed by subsequent retro-aldol condensation, and finally to produce methyl lactate in high yields. The conversions of polysaccharides such as starch and cellulose are much more challenging than those of monosaccharides and thus longer reaction time, as well as adding water co-solvent to facilitate the hydrolysis, was beneficial. Overall, this “one-pot” process using the Zr-SBA-15 catalyst and near critical methanol solvent is efficient and environmentally-friendly to produce ML from cellulosic biomass feedstocks.

Acknowledgement

This material is based upon work supported by the National Science Foundation under Grant No. CBET 1337017. The authors would like to thank Dr. Jacob Warner of the University of Minnesota Characterization Facility for the SAXS measurements, Dr. Steven Spain for the support of the analytical instruments in the Shared Instrumentation Laboratory (SIL) in Chemistry department of UNR, and Dr. Mojtaba Ahmadiantehrani in the Chemical and Materials Engineering Department for the TEM test.

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Fig. 1. Comparison of different catalysts towards the conversion of xylose in methanol. Reaction conditions: 240°C, 1h, 400psi N₂, 0.2 g xylose loading, 0.1 g catalyst.
ML: Methyl lactate, GADMA: Glycolaldehyde dimethyl acetal,
MG: Methyl glycolate, MLE: Methyl levulinate.

Fig. 2. Temperature-programmed desorption of ammonia (NH₃-TPD) for Zr-SBA-15 materials with different Si/Zr molar ratios. All materials were synthesized at the hydrothermal temperature of 100°C.

Fig. 3. Comparison of different Zr^{4+} ion loading on SBA-15 towards the conversion of xylose in methanol. Reaction conditions: 180°C, 60 min, 400 psi initial N_2 pressure, 0.2 g xylose, and 0.1 g catalyst. ML: Methyl lactate, GADMA: Glycolaldehyde dimethylacetal.

Fig. 4. Small-angle X-ray scattering patterns of Zr-SBA-15 materials with different Si/Zr molar ratios. All materials were synthesized at the hydrothermal temperature of 100°C.

Fig. 5. Effect of temperature on the yields liquids-phase products of xylose conversion with the Zr-SBA-15 catalyst in methanol. Reaction conditions: (a) 1 hour, 400 psi initial N₂ pressure, 0.2 g xylose, and 0.1 g catalyst; (b) 10 hours, 400psi N₂, 0.2 g xylose, and 0.1 g catalyst. ML: Methyl lactate, GADMA: Glycolaldehyde dimethylacetal, MG: Methyl glycolate, MLE: Methly levulinate.

Fig. 6. Effect of reaction time on the yields liquids-phase products of xylose conversion with the Zr-SBA-15 catalyst in methanol. Reaction conditions: 240 °C, 400 psi initial N₂ pressure, 0.2 g xylose, and 0.1 g catalyst. ML: Methyl lactate, GADMA: Glycolaldehyde dimethylacetal, MG: Methyl glycolate, MLE: Methly levulinate.

Fig. 7. Effect of catalyst loading on the yields of liquids-phase products of xylose conversion with the Zr-SBA-15 catalyst in methanol. Reaction conditions: 240°C, 1 hour, 400 psi initial N₂ pressure, 0.2 g xylose. ML: Methyl lactate, GADMA: Glycolaldehyde dimethylacetal, MG: Methyl glycolate, MLE: Methyl levulinate.

Fig. 8. Nitrogen adsorption–desorption isotherms of the Zr-SBA-15 materials; inset is the pore size distribution determined by NLDFT model for adsorption branch for N_2 on silica at 77K (cylindrical pore model).

Fig. 9. Re-use of the Zr-SBA-15 catalyst in the conversion of xylose. The spent catalysts were not regenerated. Reaction conditions: 240°C, 1 hour, 400 psi initial N₂ pressure, 0.2 g xylose, 0.1 g catalyst. ML: Methyl lactate, GADMA: Glycolaldehyde dimethylacetal, MG: Methyl glycolate, MLE: Methyl levulinate.

Fig. 10. High-resolution transmission electron microscopy (HRTEM) image of Zr-SBA-15: (a) fresh sample; (b) spent sample after five consecutive runs.

Table 1. Comparison of the effect of different pore sizes of Zr-SBA-15 on the catalytic conversion of xylose to methyl lactate in methanol solvent.

Entry	Feedstock	Catalyst	Conversion	Solid residue	Carbon Yield/%				
					ML	GDA	MG	MLE	Furfural
1	Xylose	Zr-SBA-15-80°C	>99%	17.4%	30.9	1.0	0.1	0.6	9.2
2	Xylose	Zr-SBA-15-100°C	>99%	10.8%	35.9	1.6	0.2	0.3	7.9
3	Xylose	Zr-SBA-15-120°C	>99%	9.2%	34.1	3.0	1.0	0.2	7.3
4	Xylose	Zr-SBA-15-150°C	>99%	6.9%	34.3	8.7	1.2	0.2	6.4

Reaction conditions: 240 °C, 1h, 400 psi N₂ pressure, 0.2g feedstock loading, and 0.1 g catalyst. ML: Methyl lactate, GADMA: Glycolaldehyde dimethylacetal, MG: Methyl glycolate, MLE: Methly levulinate.

Table 2. The physicochemical properties of Zr-SBA-15 silicates.

Catalyst ^a	BET Surface area ^b / m ² g ⁻¹	Pore volume determined by NLDFT model ^c / cm ³ g ⁻¹	Pore size determined by NLDFT model ^c / nm	Acid strength NH ₃ Quantity (mmol/g)
SBA-15-100°C	876	0.998	7.0	0.02
Zr-SBA-15-80°C	988	1.275	7.6	0.65
Zr-SBA-15-100°C	841	1.357	9.1	0.72
Zr-SBA-15-120°C	618	1.384	9.8	0.69
Zr-SBA-15-150°C	393	1.215	10.6	0.51

^aThe mole ratio of Si/Zr is 20 for the catalysts.

^bBET surface area calculated using the BET (Bruanauer-Emmett-Teller) equation at relative pressures between 0.05 and 0.25 using the adsorption branch.

^cCylindrical pore model applied for N₂ adsorption on silica at 77K for the adsorption branch.

Table 3. Comparison of the conversion of different carbohydrate feedstocks with the Zr-SBA-15 catalyst in methanol and/or water solvents.

Entry	Feedstock	Catalyst	Time/ h	Solvent	Carbon Yield/%					
					ML	GADMA	MG	MLE	Furfural	HMF
1	Xylose	/	1h	Methanol	8.1	7.9	6.3	/	/	/
2	Xylose	Zr-SBA-15	1h	Methanol	35.9	1.6	0.2	/	/	/
3	Xylose	/	1h	Water	3.0(Lactic acid)	/	/	/	21.2	/
4	Xylose	Zr-SBA-15	1h	Water	5.9(Lactic acid)	/	/	/	42.3	/
4	Glyceraldehyde	/	1h	Methanol	19.9	2.3	2.9	/	/	/
5	Glyceraldehyde	Zr-SBA-15	1h	Methanol	78.8	2.5	0.8	/	/	/
6	Dihydroxy acetone	/	1h	Methanol	29.5	1.9	3.3	/	/	/
7	Dihydroxy acetone	Zr-SBA-15	1h	Methanol	84.5	1.9	0.9	/	/	/
8	Pyrvaldehyde	/	1h	Methanol	64.5	0.7	0.2	/	/	/
9	Pyrvaldehyde	Zr-SBA-15	1h	Methanol	98.7	0.8	0.2	/	/	/
10	Glycoaldehyde	/	1h	Methanol	3.9	32.6	0.7	/	/	/
11	Glycoaldehyde	Zr-SBA-15	1h	Methanol	61.3	8.4	0.6	/	/	/
12	GADMA	Zr-SBA-15	1h	Methanol	24.0	/	0.2	/	/	/
13	Xylose	Zr-SBA-15	6h	Methanol	40.8	0.6	0.5	2.7	3.2	/
14	Glucose	Zr-SBA-15	6h	Methanol	37.3	0.6	1.0	1.3	0.9	0.2
15	Sucrose	Zr-SBA-15	6h	Methanol	39.5	0.4	0.3	2.5	1.6	2.2
16	Fructose	Zr-SBA-15	6h	Methanol	44.1	0.7	0.6	3.1	1.7	1.7
17	Glactose	Zr-SBA-15	6h	Methanol	14.8	0.8	0.1	7.2	0.9	2.1
18	Mannose	Zr-SBA-15	6h	Methanol	31.3	1.2	0.3	8.9	1.3	1.6
19	Arabinose	Zr-SBA-15	6h	Methanol	33.4	1.3	0.5	5.4	3.7	0.1
20	Cellobiose	Zr-SBA-15	10h	Methanol	24.3	0.9	0.3	4.8	1.9	2.1
21	Cellobiose	Zr-SBA-15	10h	95% Methanol	26.4	1.6	0.1	3.1	2.3	1.3
22	Cellulose	Zr-SBA-15	10h	Methanol	16.7	0.1	0.1	0.7	0.2	0.7
23	Cellulose	Zr-SBA-15	10h	95% Methanol	28.1	0.3	0.4	2.0	1.8	1.0
24	Starch	Zr-SBA-15	10h	Methanol	24.1	1.4	0.1	0.9	0.1	0.2
25	Starch	Zr-SBA-15	10h	95% Methanol	26.8	0.7	0.2	1.1	0.6	1.5

Reaction conditions: 240 °C, 400 psi initial N₂ pressure, 0.2 g biomass substrate, and 0.1g Zr-SBA-15. ML: Methyl lactate, GADMA: Glycolaldehyde dimethyl acetal, MG: Methyl glycolate, MLE: Methyl levulinate.

Scheme 1. Proposed reaction mechanism for the conversion of xylose to methyl lactate and other intermediate and final products in methanol solvent with the Zr-SBA-15 catalyst.

Graphical abstract