



# 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.

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## 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 isomorphous 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

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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 with four oxygen atoms. Zirconium atoms have a coordination number of 7 or 8 in zirconia materials. When replacing  $\text{Si}^{4+}$  with  $\text{Zr}^{4+}$ , 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]. Hanefeld and co-workers found that Zr-TUD-1 with zirconium ion incorporated in three-dimensional mesoporous TUD-1 silicate possesses predominately Lewis acidity [33,34].

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 [35–39]. Various strategies to produce lactic acid esters have been established including both fermentative processes [40] and catalytic transformations [41,42]. 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. [43,44] 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-h reaction time. With sucrose as the substrate, the ML yield reached a record high of 68%, while when the alkali ion of  $\text{K}_2\text{CO}_3$  was added to the solvent mixture, the ML yield was further promoted to 75% at 170 °C [45]. Carlos reported that with the Sn-MCM-41 which has an atomic ratio of  $\text{Si}/\text{Sn} = 55$ , a 43% yield of ML was produced from the conversion of glucose after 20 h at 160 °C [46]. The carbon-silica composite grafted Sn(IV) showed well-balanced Lewis/Brønsted acidity and yielded 45% ML from the conversion of sucrose in methanol [47]. Sn-MWW zeolite was also demonstrated to be an effective and selective catalyst for the direct conversion of mono- and disaccharides to ML [48]. 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 [49]. Solid base catalysts, including hydrotalcites [50] and magnesium oxide [51], and supported noble metal catalysts [41] 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 [52–61]. 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 [62–65]. Methanol, a small and highly polar molecule, still exhibits weak hydrogen bonding even at the critical temperature ( $T_c = 239.4$  °C) [66,67], 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 ( $T < 240$  °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 (40 wt% 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  $\mu\text{m}$ ) 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 Ref. [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 h 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 h 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 h. The solid product was filtered with mild washing, dried at 100 °C overnight, and calcined in flowing air at 550 °C for 6 h. The  $x$  (in Zr-SBA-15- $x$ - $y$ °C) represents the mole ratio of Si/Zr, and 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°. Data were typically collected over 30 s at a temperature of 20 °C. The X-ray source was Cu  $K\alpha$  radiation with a wavelength of 1.54 Å, which was generated by a Rigaku Ru-200BVH rotating anode. Measurements were made

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