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Research Article

Production of lactic acid derivatives from sugars over post-synthesized Sn-Beta zeolite promoted by WO₃



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ABSTRACT

Various metal oxides were used as co-catalysts to improve the production of alkyl lactate over Sn-Beta-P. WO₃ exhibited the best promotion effect. The yield of MLA increased from 25% (6.5 g L^{-1}) over Sn-Beta-P (0.2 g) to 52% (13.4 g L⁻¹) over WO₃ (0.1 g) and Sn-Beta-P (0.1 g) at 160 °C for 5 h and 3.1 wt% of glucose concentration. MLA yield of 38% was attained even at glucose concentration of 10 wt% and the space-time yield reached 7.1 g $L^{-1}h^{-1}$. The action mechanism of WO₃ was investigated. Fine WO₃ particles adsorbed on surface of Sn-Beta-P in reaction media and decreased the silanol defects of Sn-Beta-P. This promotes retro-aldol of fructose, the rate-determining step of whole reaction, thus facilitated the formation of MLA. Kinetic studies indicate that the presence of WO3 decreased the activation energy of the retro-aldol of fructose. The binary solid WO3 and Sn-Beta-P is recyclable.

1. Introduction

Lactic acid (LA) and its derivatives have wide applications in food, cosmetic, pharmaceutical and chemical industries (Lu et al., 2017; Mäki-Arvela, Simakova, Salmi, & Murzin, 2014; Panesar, Kennedy, Gandhi, & Bunko, 2007). In food industry, lactic acid can be applied as acidifying agent, flavouring, antimicrobial substance, and preserver in production of food (Djukić-Vuković et al., 2012). Meanwhile, the derivative poly(lactic acid), a promising biodegradable polymer, can be used to produce active food packaging which can prolong the shelf life and/or improve the sensory or safety properties while preserving the quality of the food (Altan, Aytac, & Uyar, 2018). Sugars including glucose, sucrose, cellobiose and so on are usually used to produce LA and its derivatives by fermentation method. Besides microbial fermentation, catalytic conversion of sugars to lactate derivatives is also attracts much attention in recent years (Mäki-Arvela et al., 2014). Glucose is the basic unit in many sugars. Conversion of glucose to LA or alkyl lactate was selected as the model reaction for sugars conversion in many reports. It is generally accepted that the catalytic conversion of glucose to LA or alkyl lactate proceeds through the isomerization of glucose to fructose, the redro-aldol of fructose to trioses, and then the isomerization of triose to LA in water or alkyl lactate in alcohol (Scheme S1) (de Clippel et al., 2012; Holm, Saravanamurugan, &

Taarning, 2010; Zhou et al., 2014); moreover, the redro-aldol of fructose to trioses is considered to be the rate-determining step (Holm et al., 2010; Orazov & Davis, 2015).

Solid Lewis acids and solid bases are two types of efficient heterogeneous catalysts for transformation of sugars to LA and alkyl lactates (de Clippel et al., 2012; Guo et al., 2013; Holm et al., 2010; Liu et al., 2011; Orazov & Davis, 2015; Pang et al., 2017; Zhang et al., 2017). Lewis acids are more active and selective than solid bases. Among Lewis acids, Sn-Beta zeolite is the most studied one, which can be prepared by the bottom-up (i.e. hydrothermal synthesis and dry gel conversion) (Chang, Cho, Wang, Wang, & Fan, 2015; Holm et al., 2010; Kang, Zhang, Liu, Qiu, & Yeung, 2013; Tolborg et al., 2014; Zhu, Xu, Jiang, Guan, & Wu, 2017), and the top-down method (post-synthesis) (Dijkmans et al., 2013; Hammond, Conrad, & Hermans, 2012; Li et al., 2011; Tang et al., 2014; Zhang et al., 2017). The post-synthesis method is simple and timesaving than the hydrothermal synthesis method; moreover, Sn-Beta zeolite with higher Sn content can be obtained. However, the post-synthesized Sn-Beta (Sn-Beta-P) zeolite usually has considerable silanol defects and thus is hydrophilic, which render it less selective for production of alkyl lactate from hexose. The yield of methyl lactate (MLA) from glucose, the most cheap and abundant C₆ monosaccharide, is about 20% over Sn-Beta-P, which is much lower than over Sn-Beta hydrothermally synthesized in F⁻ media (Tolborg

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et al., 2015; Yang et al., 2017). In view of the virtues of the postsynthesis method, it is highly desirable that Sn-Beta-P can give high selectivity for alkyl lactate from hexose. Tolborg et al. incorporated alkali salts to Sn-Beta-P or to the reaction medium to increase MLA yield from hexose (Elliot, Tolborg, Madsen, Taarning, & Meier, 2018; Tolborg et al., 2015). It is speculated that the improvement in MLA selectivity could arise from the neutralization of Brønsted acidity of defects in the framework, thereby promoting the retro-aldol of hexose and limiting the formation of byproducts. Our previous work indicates that recrystallization of Sn-Beta-P in the presence of low concentration of tetraethyl ammonium hydroxide can heal silanol defects and at the same time generate hierarchical porosity. Thus, the retro-aldol of fructose to trioses was facilitated and the yield of MLA improved (Yang et al., 2017). Orazov and Davis combined MoO3 with Sn-MFI and realized the conversion of ketohexoses to alkyl lactates at moderate temperature (about 100 °C) (Orazov & Davis, 2015). But, the action mechanism of MoO₃ was not revealed; moreover, the yield of alkyl lactate decreased drastically with increasing the substrate concentration with this catalyst system. When the content of fructose in ethanol increased from 1 wt% to 5 wt%, the yield of ethyl lactate reduced from 65.7% to 21.0%.

In the present work, metal oxide is used to modify the selectivity and activity of Sn-Beta-P for retro-aldol of hexose to alkyl lactate which is the precursor for producing high quality LA by hydrolysis. Various metal oxides were tested for the retro-aldol of glucose to MLA, and WO₃ exhibited the best promotion effect on the production of MLA. The action mechanism of WO₃ was revealed through kinetic studies and controlled experiments. Additionally, various reaction conditions were optimized to improve the productivity of MLA.

2. Materials and methods

2.1. Materials

Metal oxides were prepared by calcination of the corresponding precursors in muffle furnace. The used materials and the detailed calcination conditions were listed in Table S1. The structure of the metal oxides was determined by XRD (Fig. S1).

2.2. Synthesis of Sn-Beta-P

Sn-Beta-P was prepared by solid-state ion-exchange method from Al-Beta ($n_{\rm Si}/n_{\rm Al}$ of 13.8) purchased from Nankai University. According to the literature (Hammond et al., 2012; Yang et al., 2017), Al-Beta was first dealuminated with HNO₃ (13 mol L⁻¹) at 100 °C for 20 h. The dealuminated Beta (deAl-Beta) was filtered, washed with deionized water and dried at 100 °C overnight. The dried deAl-Beta was ground with SnCl₄·5H₂O in agate mortar for 1 h; then the mixture was dried at 100 °C overnight and calcined at 550 °C for 6 h to obtain Sn-Beta-P. The nominal Sn content is 2 wt%.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were obtained with a PANalytical X'pert PRO instrument with Cu K α radiation ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) was performed on JEOL JSM-6700F. The adsorption/desorption isotherms were measured with a Quantachrome Autosorb using N₂ as adsorbate at -196 °C. Sn-Beta-P was outgassed at 300 °C for 3 h before measurements. Total surface area was calculated on the basis of Brunauer-Emmet-Taller (BET) method. Micropore size distribution was calculated based on Horvath-Kawazoe (HK) method, and mesopore size distribution was calculated from the desorption branch of the isotherm with Barret-Joyner-Halenda (BJH) method. Ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) were carried out on an Agilent Technologies Cary Series UV–vis-NIR spectrophotometer. Induced coupled plasma-atomic

emission spectroscopy (ICP-AES) was applied to determine the W content in methanol. The acid properties of the catalyst were measured by FT-IR spectra with pyridine adsorption on a spectrometer of Bruker Tensor II. First, the catalyst was treated at 450 °C for 3 h under evacuation condition. By using air as the background, FT-IR spectrum in the hydroxyl stretching vibration region was collected after cooling down to room temperature. After collection of another IR spectrum for using as background for the following test, pyridine gas was charged into the pool. After adsorption saturation, pyridine molecules were desorbed at designated temperature for 30 min, and pyridine-FT-IR spectrum was collected.

2.4. Reaction tests

Retro-aldol reaction of sugars was performed in a stainless autoclave (80 mL) with PTFE liner. Methanol (15 mL), sugar and catalyst were charged into the reactor in turn under stirring. After the autoclave was sealed, the atmosphere in the reactor was replaced four times with N_2 and then $0.5 \text{ MPa} N_2$ was charged. The reactor was heated to the desired temperature with a heating rate of $\sim 4 \,^{\circ}\text{Cmin}^{-1}$ and kept the temperature for a designed time. When the reaction was over, the reactor was quenched in ice-water. The reaction mixture was centrifuged and the obtained liquid was collected and adjusted to constant volume with methanol for GC and HPLC analyses. GC analysis was carried out on a Shimadzu GC-2014C equipped with an FID detector and naphthalene was used as the internal standard. LC analysis was performed on a Shimadzu LC-20AT HPLC analysis system equipped with a refractive index detector (RID-10A) and an Aminex HPX-87H column (300 mm \times 7.8 mm). H_2SO_4 (0.005 M, 0.5 mL min $^{-1})$ was used as the mobile phase and the column temperature was 60 °C. It is noted that the yields of retro-aldol products are carbon yields.

3. Results and discussion

3.1. Characterization of Sn-Beta-P

XRD pattern (Fig. S2a) shows that Sn-Beta-P has a typical BEA structure and no other crystalline phase is observed. SEM image indicates that Sn-Beta-P is lump-like aggregates in micrometer size. The result of N₂ physisorption (Fig. S2b, S2c, S3 and Table S2) shows that Sn-Beta-P has micropore diameter of 0.78 nm; additionally, some mesopores with volume of $0.15 \,\mathrm{mL \, g^{-1}}$ present due to dealumination. UV-vis DRS (Fig. S2d) of Sn-Beta-P has a strong absorption at 200 nm, which is assigned to the charge transfer of O^{2-} to tetrahedrally coordinated Sn⁴⁺ in the framework positions (Dijkmans et al., 2013; Yang et al., 2017). The framework Sn⁴⁺ sites generated strong Lewis acid sites as shown in Fig. S2e, which interact with pyridine giving the absorption band at *ca*. 1450 cm⁻¹ (Tang et al., 2014). Sn-Beta-P has also a very small amount of Brønsted acid sites (ca. 1550 cm^{-1}) deriving from residual framework Al (Yang et al., 2017). The band at around 1490 cm⁻¹ is ascribed to Lewis and Brønsted acid sites (Tang et al., 2014). These characterization results confirm that Sn-Beta-P zeolite was successfully prepared.

3.2. Screening metal oxides as promoter

Metal oxides including MgO, TiO₂, ZrO₂, NiO, CuO, ZnO, MoO₃ and WO₃ were selected as promoter for the conversion of glucose to MLA (Fig. S4). The products of glucose conversion were identified by HPLC and GC–MS. Besides the main product MLA and the addition products of the intermediate pyruvaldehyde (PA) with methanol which are denoted as other C₃ products (Yang et al., 2017), low concentration of glycolaldehyde (C₂ product) and erythrose (C₄ product) was also detected. In the blank experiment, the total yield of C₃ products is no more than 10% though 39% of glucose was converted. The yield of MLA and other C₃ products both increased significantly to 25% under the

Table 1				
Isomerization	of glucose	in	methanol.	1

Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)				
				Fructose	Mannose	MG	MLA	Other C ₃
WO ₃	110	1	12	0	7	0	2	0
	130	1	19	0	13	0	0	0
	130	10	41	0	14	0	0	4
	160	1	46	0	16	0	0	3
Sn-Beta-P	90	1	65	39 (60)	0	7	2	0
	110	1	95	58 (61)	0	8	3	6
	130	1	99	42 (42)	0	10	9	11
$Sn-Beta-P + WO_3^2$	90	1	40	26 (65)	0	5	2	2
	110	1	75	30 (40)	0	12	9	10
	130	1	98	21 (21)	0	10	28	20

¹ Reaction conditions: glucose (0.37 g), catalyst (0.2 g), methanol (15 mL), N₂ (0.5 MPa). The value in the parenthesis is the selectivity of fructose.

 2 The binary solids are composed of Sn-Beta-P (0.1 g) and WO₃ (0.1 g).

catalysis of Sn-Beta-P, confirming the ability of aldose-ketose isomerization and retro-aldol condensation of this Lewis acid catalyst. It is reported that the formation of other C_3 products is catalyzed by Brønsted acid sites (Pescarmona et al., 2010; Saravanamurugan & Riisager, 2013; Taarning et al., 2009). Sn-Beta-P had a few Brønsted acid sites (Fig. S2e) generated from the residual Al species (Yang et al., 2017). So, the production of other C_3 was attributed to the presence of these Brønsted acid sites. Over metal oxide alone (Fig. S5), the yields of MLA and other C₃ products were much lower than over Sn-Beta-P. However, when combining metal oxide with Sn-Beta-P, the systems presented different behaviors. Addition of MgO as a promoter, the yield of MLA was unchanged, but the yield of other C₃ decreased remarkably. MgO is a typical solid base. During the reaction, a small amount of MgO would leach into the solution (Liu et al., 2011), which interacted with the Brønsted acid sites of Sn-Beta-P and thereby limited the formation of other C₃ products. The addition of TiO₂ and ZrO₂ reduced both MLA and other C₃ products. The other metal oxides including NiO, CuO, ZnO, MoO₃ and WO₃ all promoted the formation of MLA, but the yield of other C₃ is similar with that over sole Sn-Beta-P except for MoO₃. In the presence of MoO₃, the formation of other C₃ products was restrained markedly. The yield of MLA increased in the presence of different promoters following the order of NiO < CuO < ZnO < $MoO_3 < WO_3$. The yields of MLA and total C_3 products reached 52% and 74% over WO₃ combined with Sn-Beta-P catalyst, respectively, which are higher than over other binary solids. Besides the C₃ products, low yields of glycolaldehyde (2.3%) and erythrose (0.7%) were detected over WO3 combined with Sn-Beta-P. Glycolaldehyde and erythrose were formed via direct retro-aldol condensation of glucose, while C₃ products mainly generated from the retro-aldol condensation of fructose intermediate (Orazov & Davis, 2015). The catalyst showed high selectivity for C₃ products, which is attributed to the excellent performance of Sn-Beta-P for aldose-ketose isomerization. It is reported that the other C₃ products, that is the addition products of PA with methanol, can be transformed to MLA through back reaction (West et al., 2010). If it can be realized, the yield of the target product MLA can be further increased. The focus of this work is the C₃ products, and the concentrations of C₂ and C₄ products are very low in the presence of Sn-Beta. So, the yields of C2 and C4 products are not given in the following section.

In a work reported by Orazov and Davis, MoO₃ combined with a Sncontaining silicate molecular sieve was reactive for retro-aldol reaction of fructose even at 100 °C, whereas tungstate species performed poorly (Orazov & Davis, 2015). It is speculated that reaction conditions, such as reaction temperature and substrate concentration, have important influence on the catalytic performance of Sn-Beta-P combined with MoO₃ and WO₃. So, we investigated further the conversion of glucose in methanol over Sn-Beta-P promoted by MoO₃ and WO₃, respectively. The results are shown in Fig. S6. Indeed, at lower temperature, Sn-BetaP combined with WO₃ is less active than that combined with MoO₃ for the conversion of glucose to MLA. But, the activity of Sn-Beta-P combined with WO₃ at low temperature gradually approaches to that of Sn-Beta-P combined with MoO₃ with the increase of glucose concentration. When the concentration of glucose is 8.5 wt% (Fig. S6c), the activity of Sn-Beta-P combined with WO₃ at ~130 $^{\circ}$ C already exceeds that of Sn-Beta-P combined with MoO₃. At glucose concentration of 8.5 wt%, 43% yield of MLA was obtained at 160 °C for 5 h over WO3 promoted Sn-Beta-P, which is much higher than over Sn-Beta-P promoted by MoO₃ (24%). WO3 promoted Sn-Beta-P catalyst gave 38% MLA yield even when the concentration of glucose was 10 wt% and the corresponding space-time yield reached $7.1 \text{ g L}^{-1}\text{h}^{-1}$. The high space-time yield is highly desirable and very favorable for practical application. In addition, it should be mentioned that MoO₃ is unstable and partially reduced by glucose during the reaction as revealed by the XRD results in Fig. S1g.

3.3. Action mechanism of WO₃

As mentioned in literature (de Clippel et al., 2012; Holm et al., 2010; Zhou et al., 2014), the conversion of glucose to alkyl lactate is a tandem reaction and comprises three main steps (Scheme S1). In order to find the exact action mechanism of WO₃ in the reaction, isomerization of glucose, retro-aldol of fructose and isomerization of triose (1,3dihydroxyacetone, DHA) to MLA were performed over WO₃, Sn-Beta-P and binary solids (WO3 and Sn-Beta-P), respectively. For isomerization of glucose in methanol (Table 1), WO3 alone shows low activity, moreover, glucose does not isomerize to fructose but epimerize to mannose. This behavior of WO₃ is similar with molybdate that is a typical catalyst for epimerization of aldose (Bílik, 1972). Sn-Beta-P was much more active for glucose conversion, which was converted quickly at moderate temperature and fructose was a main product. The excellent performance of Sn-Beta-P for glucose isomerization to fructose is ascribed to the abundant Si-OH defects (Jiang et al., 2018). This point is important for production of alkyl lactate, because two trioses can be obtained from retro-aldol of fructose. Increasing temperature to 130 °C, considerable retro-aldol products formed and the amount of fructose decreased. This confirmed the ability of Sn-Beta-P for retro-aldol of fructose. In addition, a certain amount of methyl glucoside (MG) was also detected due to that Sn-Beta-P has a few Brønsted acid sites. The Sn-Beta-P combined with WO3 is less active than solo Sn-Beta-P for glucose conversion. Fructose is still a main product at lower temperature, but its selectivity is lower than over solo Sn-Beta-P at comparable conversion of glucose. It means that the presence of WO₃ is unfavorable for isomerization of glucose to fructose. In order to further confirm this point, the amount of WO3 was varied in the isomerization of glucose to fructose. Fig. S7 indicates that the conversion of glucose and the yield of fructose decreased with increasing the amount of WO₃. Contrarily, the

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Table 2			
Retro-aldol	of fructose	in	methano

Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)			
				MLA	Other C ₃	MLE	MG
WO ₃	140	5	31	3	4	4	0
	150	5	49	4	4	5	0
	160	5	80	4	6	5	3
Sn-Beta-P	120	1	46	4	6	0	7
	120	5	69	8	11	4	10
	160	5	99	25	21	6	0
$\text{Sn-Beta-P} + \text{WO}_3^2$	120	1	50	11	11	0	9
	120	5	70	18	17	0	8
	160	5	99	50	24	3	0

Reaction conditions: fructose (0.34 g), catalyst (0.2 g), methanol (15 mL), N₂ (0.5 MPa).

The binary catalyst is composed of Sn-Beta-P (0.1 g) and WO₂ (0.1 g).

selectivity for retro-aldol products increased significantly over the binary solids. At 130 °C for 1 h, the yield of total C₃ products reached 48%.

The performance of WO₃, Sn-Beta-P and the binary solids for the retro-aldol reaction of fructose in methanol is given in Table 2. The activity of WO₃ for the retro-aldol reaction of fructose is very low, although it is an acid material (Fig. S8); the yield of total C₃ products was no more than 10% even at 160 °C for 5 h. A small amount of methyl levulinate (MLE) was also detected, which derived from fructose dehydration, a competitive reaction of the retro-aldol of fructose. This implies that WO3 in methanol can afford Brønsted acid sites because fructose dehydration is generally catalyzed by Brønsted acid (Jiang et al., 2018). Sn-Beta-P alone shows much higher activity for the retroaldol reaction of fructose than WO3 alone. 46% yield of total C3 products was achieved at 160 °C for 5 h. For the Sn-Beta-P combined with WO3, the conversion of fructose was comparable to that over Sn-Beta-P alone, but the selectivity for the retro-aldol products increased remarkably. At 160 °C for 5 h, 74% yield of total C3 products was obtained. The above results proved that Sn-Beta-P combined with WO₃ promoted the retro-aldol reaction of fructose, the rate-determining step of glucose to alkyl lactate.

The kinetics of the retro-aldol of fructose over Sn-Beta-P combined with WO3 was studied and compared with Sn-Beta-P alone (Fig. S9 and Fig. S10). The retro-aldol of fructose fitted well with the pseudo-firstorder reaction kinetics, which is consistent with our previous report (Yang et al., 2017). Over Sn-Beta-P combined with WO₃, the apparent activation energy is 91 kJ mol^{-1} (Fig. S11a), which is lower than that over Sn-Beta-P alone (131 kJ mol⁻¹) (Fig. S11b). This means that WO₃ as a promoter changed the formation pathway of MLA, lowered the activation energy, and thus facilitated the formation of MLA.

The performance of the Sn-Beta-P, WO₃, and the binary solids for

isomerization of DHA to MLA was also investigated (Fig. 1). The activities of the three catalysts follow the order of Sn-Beta-P > the binary solids $> WO_3$. It shows that the addition of WO₃ has an adverse effect on the conversion of DHA to MLA.

Based on the above results, it can be concluded that: (1) WO_3 alone shows low activity in all the three steps including isomerization of glucose, retro-aldol of fructose and isomerization of DHA to MLA. (2) Compared to Sn-Beta-P alone, addition of WO₃ has a significant promotion effect on the retro-aldol of fructose, while has adverse effects on both the isomerization reactions of glucose to fructose and DHA to MLA. Considering the poor performance of WO₃ alone in the retro-aldol of fructose to C₃ products, the promotion effect of WO₃ might be realized through the interaction between WO₃ and Sn-Beta-P. In other words, WO3 might modify some properties of Sn-Beta-P. To investigate the promotion mechanism, control experiments were carried out. First, WO₃ was added to methanol. After treatment at 160 °C for 5 h, WO₃ was removed by centrifugation. Then, Sn-Beta-P and glucose were added to the treated methanol for reaction. The result is listed in Table 3 (entry 1). 49% of MLA yield and 20% of other C₃ yield were obtained, which are comparable to that over the Sn-Beta-P combined with WO₃ (52% MLA yield and 22% other C₃ yield as shown in Fig. S4). This indicates the promotion effect also existed when WO3 treated methanol and Sn-Beta-P were combined. Similar phenomenon also presents in MoO₃ catalytic system (Table 3, entry 2). ICP results indicate 99.9 mg L^{-1} of W element and 503 mg L^{-1} of Mo element exist in the reaction solution. Is the W species in treated methanol homogeneous or heterogeneous? If the W species in treated methanol is homogeneous, there would be a precipitate-dissolution equilibrium in the system. In this case, the concentration of W species in methanol would be unrelated to the addition amount of WO_3 as long as the presence of solid WO_3 in methanol. However, as shown in Fig. S12, there is an obvious relationship



Fig. 1. Isomerization of DHA to MLA over WO₃, Sn-Beta-P and Sn-Beta-P combined with WO₃. Reaction conditions: DHA (0.34 g), catalyst (0.2 g), methanol (15 mL), N_2 (0.5 MPa), 1 h. The binary solids are composed of Sn-Beta-P (0.1 g) and WO_3 (0.1 g).

Table 3 Results of control experiments.¹

Entry	Catalytic system	Yield (%)		
		MLA	Other C ₃	
1	WO ₃ treated methanol + Sn-Beta-P	49	20	
2	MoO ₃ treated methanol + Sn-Beta-P	41	11	
3	Treated Sn-Beta-P + fresh methanol	47	22	
4	WO ₃ /Sn-Beta-P	49	14	

 1 Reaction conditions: glucose (0.37 g), catalyst (0.2 g), methanol (15 mL), N_2 (0.5 MPa), 160 °C, 5 h.

between WO₃ amount and MLA yield. Thus, the W species in methanol should be heterogeneous. Probably, some ultra-small particles that stripped off from the bulk WO₃ adsorbed on Sn-Beta-P, and modified the properties of Sn-Beta-P, which led to the promotion effect on the catalytic performance. Another control experiment was carried out to prove this inference. First, methanol was treated with WO₃ at 160 °C for 5 h. After removing WO₃, Sn-Beta-P was added to the treated methanol. The mixture was treated at 160 °C for 5 h, and then Sn-Beta-P was separated out. Finally, the treated Sn-Beta-P and glucose were added to fresh methanol for reaction. The result is listed in entry 3 in Table 3. 47% of MLA and 22% of other C3 yield were obtained. This result is comparable to that of catalytic system of WO3 treated methanol and Sn-Beta-P in entry 1 in Table 3. It suggests that the promotion effect of WO3 was realized by modification of Sn-Beta-P through adsorption of heterogeneous ultra-small WO₃ particles on Sn-Beta-P. Inspired by the result, we prepared a sample with highly dispersed W species. W species was loaded on Sn-Beta-P by incipient wetness impregnation method with an aqueous (NH₄)₁₀W₁₂O₄₁·xH₂O solution. After drying, the solid was calcined at 450 °C for 2 h. The sample was denoted as WO₃/Sn-Beta-P and W/Sn molar ratio was controlled at unit. As expected, the catalytic performance of WO₃/Sn-Beta-P (Table 3, entry 4) is similar with the controlled experiments and comparable to that of Sn-Beta-P combined with bulk WO₃. The result confirmed the promotion effect of heterogeneous small particles of WO3 on the catalytic performance of Sn-Beta-P.

To investigate the effect of WO₃ on the acid properties of Sn-Beta-P, FT-IR spectra of pyridine adsorbed on Sn-Beta-P with/without small particles of WO₃ were collected (Fig. 2a). For treated Sn-Beta-P (Table 3, entry 3), the absorption bands at 1451 cm⁻¹ and 1612 cm⁻¹ corresponding to strong Lewis acid sites shifted to lower wavenumber (1447 cm⁻¹ and 1607 cm⁻¹) compared to Sn-Beta-P, which indicates the presence of WO₃ weakened the strength of Lewis acid. This is disadvantageous for all the three steps of glucose to MLA. Fig. 2b shows the FT-IR spectra of the two samples in the hydroxyl stretching

vibration region. The amount of silanols on the surface of Sn-Beta-P decreased significantly after interaction with ultra-small WO₃ particles. The interaction between metal oxides, such as WO₃ and MoO₃, with -OH groups is a common phenomenon (Li, Pidko, & Hensen, 2016; Miliordos, Caratzoulas, & Vlachos, 2017). It has been reported that silanols are favorable for the isomerization of glucose to fructose (Bermejo-Deval, Orazov, Gounder, Hwang, & Davis, 2014; Jiang et al., 2018; Li, Pidko, & Hensen, 2014; Rai, Caratzoulas, & Vlachos, 2013), and DHA to MLA (Yang et al., 2016), but disadvantageous for the retroaldol of hexose to alkyl lactate (Elliot et al., 2018; Tolborg et al., 2015; Yang et al., 2017, 2018). Josephson has reported that silanols facilitate the fructose etherification which is undesirable in conversion of glucose to MLA (Josephson et al., 2018). Thus, the isomerization of glucose to fructose and DHA to MLA was restrained over WO3 combined Sn-Beta-P catalyst due to the decrease in Lewis acidity and silanols; whereas for the retro-aldol of fructose the decrease of silanols is favorable, and the yield of MLA was improved. The promotion effect of WO3 on the formation of MLA from glucose over Sn-Beta-P was summarized in Scheme S2.

To further prove the role of WO₃ in conversion of glucose to MLA, alkali ions, which were reported to be good promoters for production of MLA from C₆ over Sn-containing silicate molecular sieves (Elliot et al., 2018; Tolborg et al., 2015), were also applied as promoters in this study. As shown in Fig. S13, KBr can improve the yield of MLA markedly over solo Sn-Beta-P; the yield of MLA was improved from 25% without KBr to the maximum of 56% at KBr concentration of 6 mmol L⁻¹. However, for binary solids of WO₃ and Sn-Beta-P, the promotion effect of KBr on the selectivity of MLA was moderate. The yield of MLA only increased from 52% without KBr to the maximum of 60% with 10 mmol L⁻¹ KBr. This result was caused by the overlapping role of WO₃ and KBr, both of which decrease silanol defects of Sn-Beta-P.

3.4. Product evolution with reaction time

The effects of reaction temperature and time on the conversion of glucose over WO₃ promoted Sn-Beta-P catalyst are depicted in Fig. S14. The yield of MLA is highly dependent on the temperature, which increased significantly with the increase of the temperature. Nevertheless, the yield of other C₃ products only slightly enhanced with the temperature. The yields of MLA and other C₃ products increased gradually with the reaction time, but too long time reduced the yields of MLA and other C₃ products slightly.

3.5. Scope of WO₃ promoted Sn-Beta-P catalyst



WO3 promoted Sn-Beta-P catalyst was also tested for transformation

Fig. 2. FT-IR spectra of Sn-Beta-P and treated Sn-Beta-P (a) after pyridine adsorption and evacuation at 150 °C for 30 min, and (b) in the hydroxyl stretching vibration region.

Table 4

Conversion of various sugars to alkyl lactates over WO_3 promoted Sn-Beta-P catalyst. 1

Entry Substrate	Solvent	Yield of alkyl lactate (mol %)
1 Glucose 2 Fructose 3 Mannose 4 Sucrose 5 Cellobiose 6 Glucose 7 Glucose	Methanol Methanol Methanol Methanol Ethanol n Butanol	52 50 50 60 9 34 22

 1 Reaction conditions: carbohydrate (containing 1.87 mmol C₆ units), Sn-Beta-P (0.1 g), WO₃ (0.1 g), methanol (15 mL), N₂ (0.5 MPa), 160 °C, 5 h.

of other C_6 carbohydrates to MLA. The results are presented in Table 4. Glucose, fructose and mannose (entries 1-3) give similar MLA vield. implying the binary catalyst can catalyze the mutual isomerization of the three carbohydrates. Sucrose (entry 4) composed of one glucose unit and one fructose unit linked by α,β -1,2-glycosidic bond gives higher MLA yield than C₆ monosaccharide. The reason is probably that the gradual degradation of sucrose made the concentration of C₆ monosaccharide in low level, which reduced the side reactions (Pang et al., 2017; Yang et al., 2018). Cellobiose (entry 5), a disaccharide, made of two glucose units through β-1,4-glycosidic bond, provides much lower MLA yield than sucrose due to the difficult depolymerization of β -1,4-glycosidic bond. With ethanol and *n*-butanol as solvents, the yields of alkyl lactates reduced. The change trend is similar with our previous reports (Yang et al., 2017, 2018). The reason can be ascribed to larger diffusion limitation in higher alcohols over Sn-Beta zeolite.

3.6. Reusability of WO₃ promoted Sn-Beta-P catalyst

The reusability of WO3 promoted Sn-Beta-P catalyst was studied (Fig. S15). From the 1st to the 3rd run, the catalyst was recovered by centrifugation, washed with methanol for three times, dried at ambient temperature and then used directly. The yields of MLA and other C₃ products unchanged in the 2nd run, but decreased dramatically in the 3rd run. The catalyst recovered from the 3rd run was calcined at 550 °C for 1 h besides washing with methanol and then used for the 4th run. The yields of MLA and other C₃ products regained. This indicates the organics deposited during the reaction restrained the performance of the catalyst. After that, the recovered catalyst was all calcined before used for the next run. The yields of MLA and other C₃ products were kept, proving the high recyclability of the binary solids. In addition, a hot filtration experiment was performed. The binary solids were separated from the reaction mixture after reaction at 160 °C for 1 h, and then the reaction proceeded for another 4 h. The yield of MLA only slightly increased from 42% to 45%, confirming the heterogeneous character of the binary catalyst. Sn-Beta-P used here is prepared without toxic fluoride and organic template, and the catalyst of Sn-Beta-P and WO₃ is recyclable. Besides, the product of MLA can be easily separated from the reaction mixture by distillation. In view of these advantages, the method developed here can be regarded as a green catalytic approach.

4. Conclusions

 WO_3 shows significant promotion effect for increasing the yield and selectivity of MLA from glucose over Sn-Beta-P; the yield of MLA increased from 25% to 52%. The space-time yield of 7.1 g L⁻¹ h⁻¹ was obtained. Fine WO₃ particles were adsorbed on surface of Sn-Beta-P in reaction media and decreased the silanol defects on Sn-Beta-P. This improves the selectivity of retro-aldol of fructose, which is the ratedetermining step of hexose conversion to alkyl lactate, and thus the yield of MLA. The promotion mechanism of WO_3 in this study is also suitable for other metal oxides, such as MoO_3 , in similar reaction system. Moreover, the binary catalyst of WO_3 and Sn-Beta-P is easily separated and recyclable.

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Declarations of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2019.03.039.

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