

Article

Catalytic Conversion of High Fructose Corn Syrup to Methyl Lactate with CoO@silicalite-1

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Abstract: Methyl lactate (MLA), a versatile biomass platform, was typically produced from the catalytic conversion of high-priced fructose. High fructose corn syrup (HFCS) is a mixture of glucose, fructose, water, etc., which is viewed as an economical substitute for fructose to produce MLA due to the much lower cost of separation and drying processes. However, the transformation of HFCS to MLA is still a challenge due to its complex components and the presence of water. In this work, the catalytic conversion of HFCS to MLA over CoO@silicalite-1 catalyst synthesized via a straightforward post citric acid treatment approach was reported. The maximum MLA yield reached 43.8% at 180 °C for 18 h after optimizing the reaction conditions and Co loading. Interestingly, adding extra 3% water could further increase the MLA yield, implying that our CoO@silicalite-1 catalyst is also capable for upgrading wet HFCS. As a result, the costly drying process of wet HFCS can be avoided. Moreover, the activity of CoO@silicalite-1 catalyst can be regenerated for at least four cycles via facile calcination in air. This study, therefore, will provide a new opportunity to not only solve the HFCS-overproduction issues but also produce value-added MLA.

Keywords: high fructose corn syrup; CoO@silicalite-1; methyl lactate; influence of water



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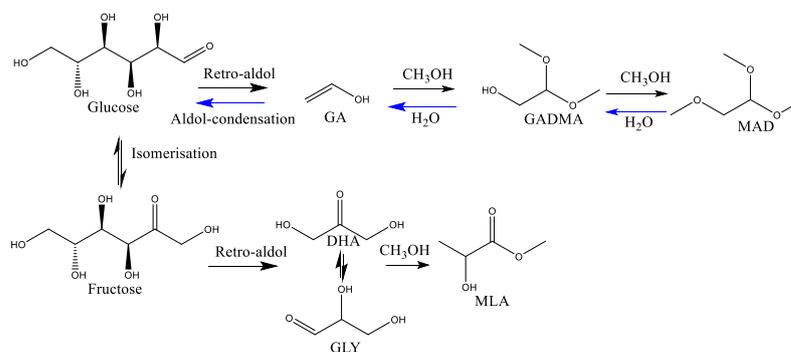


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1. Introduction

Today's world chemicals and fuels are mainly produced from fossil fuel resources, which are non-renewable with limited stocks and release a large amount of CO₂ during their consumption. Biomass is one of the promising candidates to replace fossil resources due to its renewable and abundant properties. Up to now, considerable efforts have been devoted to the efficient conversion of biomass to high value-added biofuels and chemicals [1]. Among biomass-derived chemicals, lactic acid (LA) and methyl lactate (MLA) have attracted considerable interest since they are not only green solvents due to their nontoxic and biodegradable properties [2,3], but also the precursors to produce polymer—polylactic acid (PLA), which is environmentally friendly and holds the potential to substitute fossil-based plastics in packaging applications [4,5]. Typically, LA is produced via a fermentation approach using sucrose and glucose as the main raw materials [6]. Compared with the fermentation process, MLA produced from the catalytic conversion of biomass holds the significant advantages with fast reaction rate and easy product separation [2]. Different monosaccharides and disaccharides could be converted to MLA with homogeneous and/or heterogeneous Lewis acid catalyst (e.g., SnCl₂-ZnCl₂, Snβ, Zr-SBA-15 et al.), which is efficient for the crucial retro-aldol reaction (Scheme 1) [7–17]. Fructose as a keto-type monosaccharide is an attractive reactant to produce MLA. However, the high cost of fructose production hinders its industrial development. Compared with fructose, glucose is more abundant and much cheaper. However, the glucose-to-MLA procedure is relatively

difficult in most reaction conditions since it requires one more step to isomerize the glucose to fructose. As reported, the catalytic conversion of glucose to MLA mainly includes three steps (Scheme 1): (1) isomerization of glucose to fructose; (2) retro-aldol reaction of fructose to 1,3-dihydroxyacetone (DHA) or glyceraldehyde (GLY); and (3) conversion of DHA or GLY to MLA [6,10,12]. The two main byproducts glycolaldehydedimethylacetal (GADMA) and methoxyacetaldehyde dimethyl acetal (MAD) are generated from glycolaldehyde (GA) derived from the retro-aldol reaction of glucose.



Scheme 1. Possible reaction pathways for the conversion of glucose and fructose to MLA and other byproducts. (GADMA, glycolaldehydedimethylacetal; MAD, methoxyacetaldehyde dimethyl acetal; DHA, 1,3-dihydroxyacetone; GLY, glyceraldehyde; MLA, methyl lactate; GA, glycolaldehyde).

Compared with monosaccharide, the industrially available high fructose corn syrup (HFCS) is a superior raw material to produce MLA. HFCS is an alternative sweetener to sucrose, and it can be made from the corn starch with the largest-scale among the immobilized biocatalytic manufacturing process [18]. Compared with fructose, the cost of separation and drying processes can be avoided with HFCS as the reactant. However, the overconsumption of HFCS is related to diabetes, obesity, and cardiovascular diseases that makes the consumption of HFCS declined seriously in recent years, resulting the overproduction of HFCS [19]. Therefore, the HFCS-to-MLA process could solve the HFCS-overproduction issues.

As reported, a certain amount of water is beneficial for the conversion of sugars to MLA [2,7,20,21] in methanol media since the solubility of sugars is enhanced by the presence of water. Hammond et al. revealed that the existence of water could dramatically improve the stability of the Sn β catalyst [22]. Also, our group found that the main side-product, GADMA, could be easier to be converted to MLA with water [20]. HFCS is the upstream product of fructose [18], which contains fructose, glucose, and a small amount of water. HFCS has been reported for the successful conversion to 5-hydroxymethylfurfural (5-HMF) in a one-pot reaction [23,24]. However, the conversion of HFCS to MLA is still rare due to the complex compounds in HFCS. Typically, the co-existence of Lewis acid and Brønsted acid is efficient for the production of MLA from monosaccharide. However, the excessive amount of Brønsted acid will lead to the occurrence of other side reaction: dehydration of monosaccharide to 5-HMF, thus, causing the inefficient isomerization of glucose to fructose [25]. Lewis acid is required for the isomerization of glucose to fructose as well as the retro-aldol reaction of fructose to MLA [7,26]. Therefore, it is more attractive to produce MLA from HFCS in a one-pot reaction over the catalyst with appropriate mixture of Lewis acid and Brønsted acid.

It has been reported that the CoO@silicalite-1 catalyst, with the ultrasmall CoO clusters inside silicalite-1 crystals structure, is a suitable candidate for the production of MLA from fructose in our previous work [15]. However, the catalyst requires complex pretreatment process (alkali-treatment and ion exchange for three times) prior to the catalytic reaction. In this work, a new c-CoO@silicalite-1 catalyst was synthesized via a one-step citric acid pretreatment rather than the complex alkali-treatment and ion exchange processes. The catalytic activity of c-CoO@silicalite-1 was investigated for the conversion of HFCS-55. The

characterizations of catalysts (powder X-ray diffraction (XRD) and nitrogen adsorption-desorption) confirmed the successful synthesis of c-CoO@silicalite-1. We also investigated the effect of catalyst loading, reaction temperature/time, reactant loading, and additional water content on the conversion of HFCS-55 to MLA. More importantly, this catalyst not only showed good catalytic activity but also gave an excellent recycling performance.

2. Results and Discussion

2.1. Catalyst Characterization

Firstly, XRD was used to study the chemical properties of synthesized c-CoO@silicalite-1 samples. The XRD patterns of the as-synthesized c-CoO@silicalite-1 with different Co loadings (c-Co_x) samples are shown in Figure 1. All of the synthesized c-Co_x samples with different Co loading showed the typical characteristic peaks of Mobil Five Instructure (MFI) zeolite structure ($2\theta = 7.9^\circ$ and 8.9° , Joint Committee on Powder Diffraction Standards (JCPDS) card No. 00-044-0002) [27], which indicated that the MFI structure was maintained after the introduction of Co and post-pretreatment with citric acid. For c-Co_{0.75} with the highest Co loading, the peak intensity of MFI decreased dramatically, indicating the partial collapse of the zeolite framework.

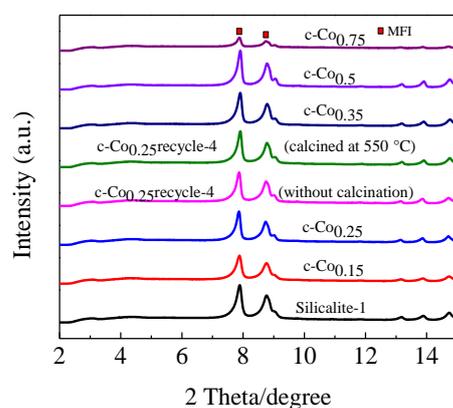


Figure 1. XRD patterns of the pristine silicalite-1 and c-Co_x.

Figure 2 and Table 1 show the nitrogen adsorption-desorption isotherms and the textural properties of the synthesized c-Co_x samples. As shown in the Figure 2, it was found that both micropore and mesopore were detected for all of the synthesized c-Co_x samples. Without Co, the blank silicalite-1 held the most abundant micropores ($417 \text{ m}^2/\text{g}$), while the amount of micropores decreased with the increase of Co loading. The amount of micropores decreased with the increase of Co loading, which showed that the incorporated Co loaded in the micropores. As for c-Co_{0.75}, the lowest microporous surface area of $68 \text{ m}^2/\text{g}$ was found due to the addition of Co and partial collapse of the silicalite-1 framework, in agreement with the results of XRD.

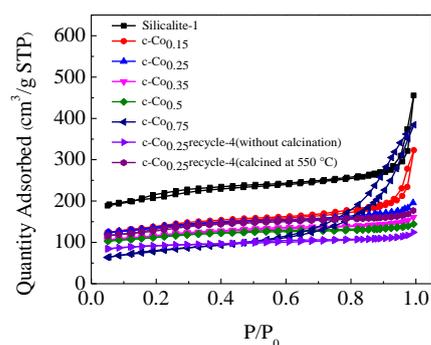


Figure 2. N₂ adsorption-desorption isotherms of pristine silicalite-1 and c-Co_x.

Table 1. Textural properties of silicalite-1 and c-Co_x.

Catalyst	BET Surface Area (m ² /g)	Micropore Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size nm
Silicalite-1	682	417	0.45	2.6
c-Co _{0.15}	451	274	0.32	2.8
c-Co _{0.25}	434	261	0.27	2.5
c-Co _{0.25} recycle-4 (without calcination)	291	209	0.17	2.4
c-Co _{0.25} recycle-4 (calcined at 550 °C)	419	215	0.25	2.4
c-Co _{0.35}	371	231	0.23	2.5
c-Co _{0.5}	360	224	0.21	2.3
c-Co _{0.75}	271	68	0.46	6.8

2.2. Catalytic Conversion of HFCS-55

The HFCS-55 contained 41.1% fructose and 32.4% glucose as detected by high performance liquid chromatography (HPLC). The ratio of fructose/(fructose and glucose) is 55.9% (Table S1). As shown in Figure S3, the water content in HFCS-55 was about 20% detected by thermogravimetry analysis (TGA). The catalytic conversion of HFCS-55 over various catalysts was studied, and the results are shown in Figure 3. In blank experiment, the conversion of sugars was 73.5% with low MLA yield of 12.8%. This is due to the fact that near-critical methanol is capable for the methanolysis of sugars [2,28]. When using silicalite-1 as the catalyst, the conversion of sugars increases to 91.4% while the MLA yield (7.9%) was slightly lower compared with blank experiment. These results indicate that the silicalite-1 itself is not an efficient catalyst for converting sugars to MLA, in agreement with the previous study [15]. For the co-doped silicalite-1 catalyst without acid pretreatment, the MLA yield was only 10.1% and increased to 43.8% when the catalyst was pretreated with citric acid. These results indicated that the acid pretreatment was necessary to active this catalyst. For c-Co_x, with the increase of Co loading, both MLA yield and HFCS-55 conversion increased firstly and then decreased. The maximum MLA yield (43.8%) with almost 100% conversion of sugars was obtained with c-Co_{0.25}, suggesting the co-existence of sufficient active sites (ultrasmall CoO clusters) and MFI zeolite framework. For c-Co_{0.75} catalyst, the yield of MLA and conversion of sugars decreased dramatically. This is due to the collapse of the framework when the Co loading is too high. It has been reported by our previous work that, with the increase amount of Co loading, the Co₃O₄ crystalline structure was discovered and the MFI structure was disappeared, suggesting that excessive Co loading destroyed the structure of MFI [15].

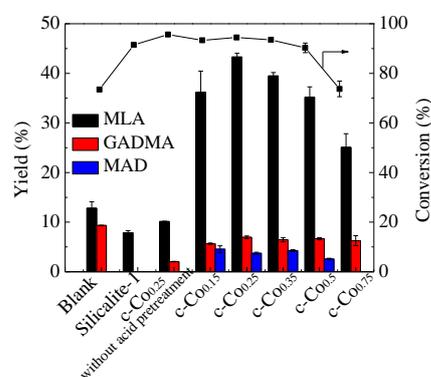


Figure 3. Catalytic conversion of HFCS-55 over c-Co_x. Reaction conditions: HFCS-55, 0.06 g; methanol, 6 mL; catalyst, 0.03 g; 180 °C; 18 h.

The reaction conditions were then optimized to maximize the yield of MLA with $c\text{-Co}_{0.25}$ as the best catalyst. Figure 4 shows the results of the effect of catalyst addition amount on the conversion of HFCS-55. As increasing the catalyst loading from 0 to 0.03 g, the conversion of sugars and yield of MLA increased gradually. When 0.01 g $c\text{-Co}_{0.25}$ catalyst was added, MLA yield increased to 30.1%, which was much higher than 12.8% from blank experiment. This clearly indicated that our $c\text{-Co}_{0.25}$ catalyst facilitated the conversion of sugars to MLA. With the increase of catalyst loading to 0.03 g, the MLA yield reached the plateau of 43.8%. However, MLA yield slightly decreased as further increasing the catalyst loading to 0.04 g, suggesting the side reactions could be also promoted in the presence of $c\text{-Co}_{0.25}$ catalyst. Therefore, a suitable amount of $c\text{-Co}_{0.25}$ catalyst was crucial for the optimized MLA production from sugars.

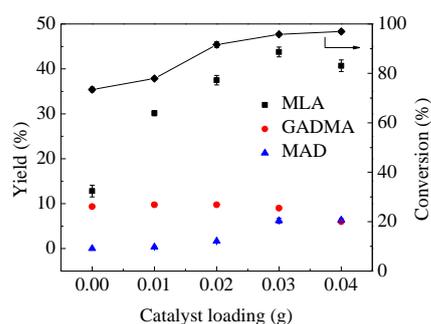


Figure 4. Effect of the $c\text{-Co}_{0.25}$ loading on the conversion of HFCS-55. Reaction conditions: HFCS-55, 0.06 g; methanol, 6 mL; 180 °C; 18 h.

Figure 5 shows the effect of reaction time and temperature on the conversion of HFCS-55. As reported before, a temperature higher than 180 °C is required for the efficient conversion of glucose to MLA [28]. A similar result was also discovered in this work for the conversion of HFCS-55. The sugars conversion (<80%) and MLA yield (<30%) were relatively low at 160 °C for all of the reaction times (3–24 h). As the reaction temperature increased to 180 °C, much higher MLA yields that up to 43.8% were obtained with a reaction time of 18 h. At 180 °C, with the increase of reaction time, the MLA yield initially increased, and then decreased steadily. The maximum yield of MLA reached 43.8% with almost total conversion of the sugars at the optimal reaction time of 18 h. When the reaction temperature increased to 200 °C, the reaction rate accelerated significantly while the MLA yield at the plateau (31.9%) was lower than that obtained at 180 °C. As shown in Figure S4, the carbon balance decreased with the increase of the reaction temperature. The higher reaction temperature was beneficial for the enhanced reaction rate, but at the same time it would also facilitate the side reactions and lead to a relatively low MLA yield. In the conversion of sugars, humins or high molecular carbonaceous species will be formed inevitably, especially at high reaction temperature [29,30]. However, these species are undetectable by HPLC or gas chromatography (GC), which are accountable for the low carbon balance.

As reported, a certain amount of water is beneficial for the catalytic conversion of sugars to produce MLA. This is due to the fact that the MAD is hydrolyzed to GADMA which is then hydrolyzed to glycolaldehyde (GA) with a certain amount of water. The produced GA could be transformed to glucose via the aldol condensation at relative higher temperature, and the glucose is subsequently converted to MLA (Scheme 1, the blue line) [20]. In this work, the total yield of GADMA and MAD keeps almost steady at 200 °C with the prolonging of reaction time (Figure 5b) since the water content in HFCS-55 is insufficient for the conversion of GADMA and MAD. Therefore, 3% additional water was added to the reaction to study the effect of water (Table 2). For the experiment with 0% additional water content, the reaction conditions were the same as Figure 3. For the experiment with 3% additional water content (3% refers to volume of water/volume of methanol), 0.18 mL water was added to the reactor before the reaction and the other

reaction conditions are the same as 0% additional water content. Comparing with the reaction without extra water, the MLA yield increased and the total yield of GADMA and MAD decreased in the presence of extra water.

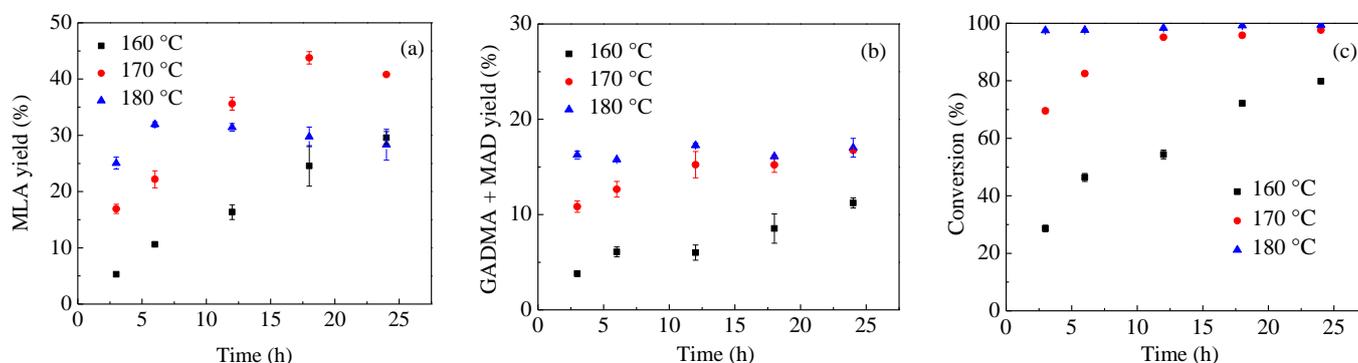


Figure 5. Effect of reaction time and temperature on the conversion of HFCS-55: (a) MLA yield, (b) GADMA + MAD yield, (c) conversion of sugars. Reaction conditions: HFCS-55, 0.06 g; methanol, 6 mL; c-Co_{0.25}, 0.03 g.

Table 2. Catalytic conversion of HFCS-55 with additional water.

Additional Water Content	MLA Yield	GADMA + MAD Yield
0	43.8%	15.2%
3% ^a	46.1%	8.3%

Reaction conditions: HFCS-55, 0.06 g; methanol, 6 mL; c-Co_{0.25}, 0.03 g; 180 °C; 18 h. ^a: 0.18 mL water was added.

The concentration of substrate is important for the industrial production, so the effect of HFCS-55 concentration was investigated and the results are shown in Figure 6. Increasing concentration of HFCS-55 from 10 to 100 g/L, the yields of MLA (43.8%~9.8%) and its side-products decreased dramatically while the conversion of sugars decreased slightly. With increase of the concentration of HFCS-55, the color of the catalyst after the reaction became darker, indicating the formation of carbonaceous species which occupied the active sites (ultrasmall CoO clusters) of the catalyst.

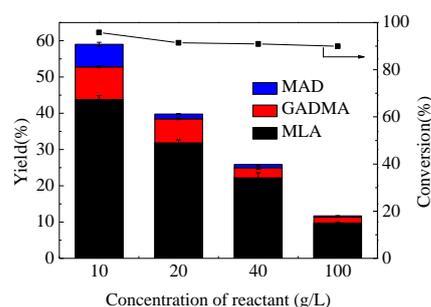


Figure 6. Effect of concentration of reactant on the conversion of HFCS-55. Reaction conditions: methanol, 6 mL; c-Co_{0.25}, 0.03 g; 180 °C; 18 h.

The catalytic stability of c-Co_{0.25} was examined using HFCS-55 as the reactant at 180 °C. In the recycling runs, the MLA yield decreased steadily when c-Co_{0.25} was reused without calcination (Figure 7). The spent catalyst without calcination showed the similar XRD patterns (Figure 1) as the fresh counterpart. However, the surface area of spent c-Co_{0.25} decreased significantly (Table 1) since carbonaceous species were formed and deposited on the surface of c-Co_{0.25} during the reaction [29]. Fortunately, after the pretreatment of spent c-Co_{0.25} at 550 °C for 6 h, the carbonaceous species could be removed, and the catalytic activity could be recovered.

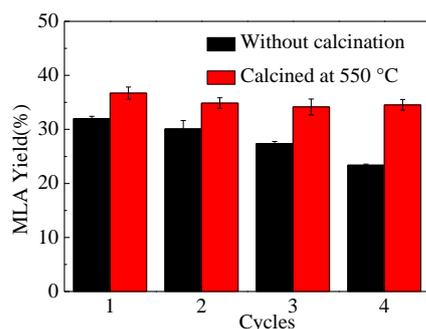


Figure 7. Stability test of c-Co_{0.25} for the conversion of HFCS-55 to MLA. Reaction conditions: HFCS-55, 0.06 g; methanol, 6 mL; c-Co_{0.25}, 0.03 g; 180 °C; 18 h.

3. Experimental Section

3.1. Catalyst Preparation

The c-Co@silicalite-1 was synthesized via the procedure reported with some modifications [15] and detailed preparation processes were shown in Supplementary Materials. Before catalytic reaction, alkali-treatment, and ion exchange for three times (totally requiring four days) were required to obtain the activated CoO@silicalite-1 in the previous work [15]. In this work, before catalytic reaction the zeolite was only pretreated with citric acid (0.5 M, 70 °C, 100 mL/g zeolite, 2 h), then washed with water and dried for 12 h (only requiring one day). The solid sample was thereafter calcined at 550 °C for 6 h to obtain c-CoO@silicalite-1. A series of synthesized catalysts was identified as c-Co_x, where x is the amount of Co(NO₃)₂·6H₂O (mmol) required in the synthesis of the catalyst.

3.2. Catalyst Characterization

Powder X-ray diffraction (XRD) was obtained by Rigaku Ultima IV (Rigaku Corp., Tokyo, Japan) with Ni-filtered monochromatic Cu K α radiation ($\lambda = 0.154$ nm) at 40 keV and 30 mA. All samples were scanned from a 2 theta range of 2–15°, with a step rate of 0.5° min⁻¹. Nitrogen adsorption-desorption was measured by American micromeritics APSP 2460 automatic specific surface and porosity analyzer (Micromeritics Corp., Norcross, GA, USA). All samples were degassed at 200 °C for 8 h, and then the adsorption and desorption test of the sample had been pretreated for 8 h at 200 °C. The specific surface area and pore volume of micropores were measured by t-plot model. The surface areas and pore volume were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was evaluated following the Barrett-Joyner-Halenda (BJH) method. Thermogravimetry (TG) was carried out using (SDT Q600, TA Instruments, New Castle, DE, USA) in N₂ atmosphere with heating rate of 10 °C·min⁻¹ from room temperature (30 °C) to 100 °C and maintained at 100 °C for 30 min.

3.3. Catalytic Conversion of HFCS-55

The composition of HFCS has been detected by HPLC and TGA, and it is named as HFCS-55 according to the ratio of fructose/(fructose and glucose).

A certain amount of HFCS-55 was dissolved in methanol to obtain solution A. 6 mL of solution A and a certain amount of c-Co_x was added to a 14-mL stainless steel reactor (Figure S2). Then the reactor was heated to the desired temperature for a fixed period of time. The conversion of reactants and yields of products were calculated based on equivalent amounts of carbon, and all of the results are the average value of three replicate experiments.

3.4. Analysis Methods

Glucose and fructose were detected by HPLC/RID (Agilent 1100, Santa Clara, CA, USA) equipped with an Aminex HPX-87H column (300 mm × 7.8 mm, BioRad Laboratories, Inc., Hercules, CA, USA). The main products MLA, GADMA, and MAD (methoxyacetalde-

hyde dimethyl acetal) were analyzed by GC/FID (GC, Agilent 7890A) with a HP-5 column (30 m × 0.32 mm × 0.25 μm, Agilent Technologies Inc., Santa Clara, CA, USA).

Conversion = (moles of starting glucose and fructose – moles of glucose and fructose at a given time)/moles of starting glucose and fructose × 100%

Yield of product = moles of carbon derived from the glucose and fructose in the product/(6 × moles of the starting glucose and fructose) × 100%

Carbon balance = (moles of carbon derived from the glucose and fructose in MLA, GADMA and MAD + moles of carbon from the unconverted sugars)/(6 × moles of the starting glucose and fructose) × 100%

3.5. Catalyst Recycles

The spent catalyst was separated from reaction mixture by filtration and was washed with methanol for three times, followed by drying at 60 °C for 12 h. For the recycling of uncalcined catalyst: The dried catalysts were directly used for the next reaction. For the recycling of calcined catalyst: The dried catalysts were calcined at 550 °C for 6 h and then they were used for the next reaction.

4. Conclusions

In this work, the catalytic conversion of HFCS-55 to MLA with CoO@Silicalite-1 catalyst synthesized via a simple acid treated method was studied. It was found that the moderate amount of CoO in silicalite-1 (c-Co_{0.25}) led to a high yield of MLA for the conversion of HFCS-55. The catalyst loading, reaction temperature and time, and concentration of HFCS-55 have also been optimized. The optimized MLA yield (43.8%) was obtained at 180 °C for 18 h with 10 g/L HFCS-55 and 0.03 g c-Co_{0.25} (6 mL methanol solution). HFCS-55 contained about 20% water, which was insufficient for the conversion of side products (GADMA and MAD) to MLA. Thus, extra water was added to the reaction and obvious higher MLA yield was detected. With calcination, c-Co_{0.25} was stable and could be reused for at least four cycles. This work provided an effective way for the high-value utilization of HFCS.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12040442/s1>. Materials and Chemicals; Detailed preparation of the catalyst; Figure S1: The Teflon-lined autoclave (a) and the Teflon cup (b); Figure S2: The photos of the stainless steel reactor (a) and heating furnace (b); Table S1: Composition of HFCS-55 detected by HPLC; Figure S3: TG analysis of HFCS-55; Figure S4: The carbon balance of the catalytic conversion of HFCS-55 under different reaction temperatures and time.

Author Contributions: Conceptualization, X.L. (Xiuyang Lu); methodology, Y.J.; software, X.L. (Xilei Lyu); validation, H.C.; formal analysis, Z.Z.; investigation, Y.J.; resources, X.L. (Xilei Lyu); data curation, X.L. (Xilei Lyu); writing—original draft preparation, Y.J.; writing—review and editing, Z.Z.; visualization, X.W.; supervision, X.L. (Xiuyang Lu); project administration, X.L. (Xiuyang Lu); funding acquisition, X.L. (Xiuyang Lu). All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are available from the corresponding author on request.

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