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Deoxydehydration and Catalytic Transfer Hydrogenation: New Strategy to Valorize Tartaric Acid and Succinic Acid to γ-Butyrolactone and Tetrahydrofuran

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Abstract: Hydrogenation of succinic acid and maleic acid produces C4 value-added chemicals such as γ-butyrolactone and tetrahydrofuran. Here, unsupported ReO_x nanoparticles transform succinic acid to γ-butyrolactone and tetrahydrofuran via catalytic transfer hydrogenation with isopropanol as a liquid phase hydrogen donor. This catalyst is also active for the sequential reaction of deoxydehydration and transfer hydrogenation in isopropanol, synthesizing renewable succinic acid and its esters from tartaric acid. One-step conversion of tartaric acid to γ-butyrolactone is achieved in a moderate yield and the possible reaction pathway is discussed.

Keywords: biomass conversion; deoxydehydration; catalytic transfer hydrogenation; γ-butyrolactone; tartaric acid; rhenium oxide

1. Introduction

Biomass is a promising renewable energy resource which may provide a sustainable route to biofuels and chemicals [1]. Fine chemicals can be produced from biomass-derived building-block compounds [2]. In 2004, the U.S. Department of Energy selected succinic acid (SA), a C4-dicarboxylic acid, as one of the bio-based key platform chemicals [3]. Renewable SA can replace maleic anhydride to synthesize many valuable chemicals including γ-butyrolactone (GBL), tetrahydrofuran (THF), and 1,4-butanediol (1,4-BDO) [4–7]. GBL has been used as a starting material for the production of N-methyl-2-pyrrolidone and other pyrrolidone derivatives. THF is a monomer of poly(tetramethylene ether) glycol (PTMEG). Both GBL and THF are also utilized as solvents. The demand for GBL and THF is increasing annually and the global market size of GBL and THF in 2018 was approximately 0.6 and 3.2 billion USD, respectively [8,9]. Thus, the preparation of renewable SA and its transformation into GBL and THF are receiving much attention.

Several methods to synthesize SA from biomass-derived compounds have been reported. Renewable SA has been typically prepared through the bio-fermentation of glucose [10,11]. However, recent breakthroughs in the biological process, costly separation, and large quantities of waste byproducts make it difficult to realize at the industrial scale [12]. SA was synthesized from furfural through thermochemical processes [13–15]. However, the C5 starting compound formed C1 byproducts such as CO_2 and formic acid. Tartaric acid (TA), a C4 sugar acid, has been proposed as an alternative resource to prepare SA without carbon loss. Tartaric acid is a naturally occurring organic acid and is generated in large quantities as a byproduct of wine-making [16,17]. MoO_x-catalyzed

hydrodeoxygenation converted TA to SA with a high yield (87%), but it required harsh conditions such as corrosive halogen, high pressure of H_2, and acetic acid [18]. Moreover, the transformation of TA to SA was achieved through a combination of deoxydehydration (DODH) and hydrogenation in two steps without harsh conditions [19]. DODH is an attractive deoxygenation reaction to prepare olefins from vicinal diols [20,21]. DODH with oxorhenium complexes converted TA to maleic acid (MA) and the resulting MA was hydrogenated over a Pt/C catalyst, producing SA with a 97% yield [19]. Previously, we reported unsupported ReO_x nanoparticles (ReO_x NPs) as an active and reusable heterogeneous catalyst to synthesize olefins from polyols through DODH with a secondary alcohol reductant. High oxidation states of Re (Re^{5+} and Re^{7+}) in the nanoparticles were involved in the DODH reaction [22]. We have found that the ReO_x NPs are not only active for DODH but also for catalytic transfer hydrogenation (CTH) at high reaction temperature (T > 200 °C) with isopropanol as a hydrogen donor. The tandem reaction of DODH-CTH over the ReO_x NPs can transform TA into SA and its ester in one step without the harsh conditions.

In addition, the ReO_x NPs further convert the prepared SA and its ester to GBL and THF through cyclization and transfer hydrogenation. The formation of GBL or THF from SA has been achieved using direct hydrogenation with H_2 gas over various monometallic or bimetallic catalysts including palladium, ruthenium, and rhenium-based catalysts [2,5–7,23]. CTH reaction using isopropanol as a hydrogen donor is a promising alternative to direct hydrogenation because the hydrogen donor is easy to handle and environmentally friendly, preventing possible hazards [24–26]. In this sense, CTH with a liquid phase hydrogen donor has been recently introduced to provide hydrogen for the hydrodeoxygenation of biomass-derived materials including 5-hydroxymethylfurfural, levulinic acid, and lignin-derived phenolics [27–30]. However, to the best of our knowledge, CTH has not been employed to prepare GBL or THF from SA or MA. Herein, we report new reaction pathways to prepare GBL and THF from renewable substrates over ReO_x NPs. First, the conversion of SA to GBL or THF through cyclization and transfer hydrogenation with ReO_x NPs is tested. Furthermore, a combination of deoxydehydration, transfer hydrogenation, and cyclization produces GBL from TA in one step.

2. Materials and Methods

2.1. Catalyst Preparation

Unsupported ReO_x NPs were prepared from ammonium perrhenate (NH_4ReO_4, Strem Chemicals) in the presence of 3-octanol (Sigma-Aldrich, St. Louis, MO, USA), as described in detail elsewhere [22]. A mixture of ammonium perrhenate (268 mg, 1 mmol) and 3-octanol (20 mL, 126 mmol) was placed in a 100 mL round bottom flask and heated at 180 °C in a pre-heated oil bath. Black ReO_x nanoparticles were synthesized after 12 h reflux in open air and isolated by centrifugation (11 000 rpm for 1.5 h). Unreacted ammonium perrhenate was removed by washing repeatedly with ethanol and hexane solution (1:1 wt %) and further centrifugation. The ReO_x NPs were dried in 120 °C oven overnight and kept in powder form for future use.

2.2. Activity Test

All activity tests were performed in a Parr batch reactor vessel. The prepared unsupported ReO_x nanoparticles (10 mg) were mixed with succinic acid (1 mmol, 118 mg, Alfa Aesar, Ward Hill, MA, USA) and isopropanol (10 mL) in the vessel. The vessel was pressurized with 15 bar of N_2 and heated to the reaction temperature for a given amount of time. The reaction time was recorded after the temperature reached the desired value. After the reaction, the spent catalyst was separated from the reaction solution. The product solution was analyzed by NMR and GC with mesitylene as an internal standard. The conversion of different substrates including maleic acid and L–(+)–tartaric acid (Alfa Aesar , Ward Hill, MA, USA) was conducted under the same conditions. The yields of TA, MA, SA, and their esters were calculated by ^{1}H NMR measured on an Agilent Technologies 400 MHz, 400-MR DD2 spectrometer. The yields of GBL and THF were quantified by gas chromatography with

a flame ionized detector (GC-FID, Agilent Technologies, Wilmington, DE, USA, 6890N with a DB-5 capillary column).

$$\text{Conversion of SA } (\%) = \frac{\text{mole of SA reacted}}{\text{mole of SA supplied}} \times 100, \quad (1)$$

$$\text{Yield for product } (\%) = \frac{\text{mole of product formed}}{\text{mole of SA supplied}} \times 100, \quad (2)$$

2.3. Characterization

The physical and chemical properties of ReO_x NPs were characterized using various characterization methods, as in our previous study [22]. In order to identify the acid type of catalyst samples, infrared spectra of catalysts were obtained with a Thermo Scientific Nicolet iS10 Fourier transform infrared spectroscopy (FT-IR) spectrometer. The catalysts were diluted with KBr, and then a baseline spectrum was obtained before pyridine introduction. Pyridine was introduced to the sample by flowing Ar through a pyridine bubbler for 10 min. To remove physisorbed pyridine, 100 sccm Ar was purged for 30 min. The spectra were obtained at room temperature.

3. Results and Discussion

3.1. Conversion of Succinic Acid (SA)

CTH reaction of succinic acid over ReO_x NPs with isopropanol as a hydrogen donor was investigated at different reaction temperatures (170–250 °C). At lower temperatures (T < 200 °C), esterification of SA gave succinic acid monoisopropyl ester (SA-ME) as a major product and a small quantity of succinic acid diisopropyl ester (SA-DE) in 1 h (Figure 1a). The CH_2 peak in the ^1H NMR spectra of SA (δ = 2.43 ppm) in DMSO-d_6 shifted downfield by 0.02 ppm (SA-ME) and 0.05 ppm (SA-DE) after esterification (Figure 2a). At 210 °C, SA conversion over ReO_x produced not only ester compounds (SA-ME and SA-DE) but also GBL. Higher GBL yields of 16% and 43% were obtained in 1 h at 230 °C and 250 °C, respectively (Figure 1a). Previously, GBL was synthesized by direct hydrogenation of SA with molecular H_2 [5–7]. The proposed mechanisms include dehydration of SA to succinic anhydride (SAN) over acid sites of the catalysts, followed by hydrogenation over metal sites [7,23]. ReO_x NPs converted SAN to 47% yield of GBL and 40% of SA-ME/DE at 250 °C in 1 h (Figure 1d). This indicates SAN as a possible intermediate in the conversion of SA to GBL while it was not detected. At 250 °C, SAN in isopropanol is susceptible to alcoholysis to SA-ME, which is further esterified to SA-DE (Scheme 1). The alcoholization and further esterification also occurred without a catalyst, but no GBL was observed (Figure 1d). This demonstrates that CTH of SAN to GBL was catalyzed by ReO_x NPs. SAN can be formed by dehydration of SA or dealcoholization of SA-ME and the resulting SAN is hydrogenated through CTH with isopropanol over ReO_x NPs (Scheme 1). Pyridine probe FT-IR shows that ReO_x NPs have both Brønsted and Lewis acid sites that can catalyze dehydration and dealcoholization (Figure 3). The bands at 1450 cm^{-1}, 1487 cm^{-1}, and 1608 cm^{-1} represent Lewis bonded pyridine. The bands at 1487 cm^{-1}, 1538 cm^{-1}, and 1631 cm^{-1} are assigned to Brønsted bonded pyridine. The previously suggested structural features of ReO_x NPs, a combination of Re=O double bonds and Re-O single bonds, can provide Lewis acid sites [22]. Lewis acidity of rhenium-based catalysts including Re_2O_7, CH_3ReO_3, and $HReO_4$ has been reported [19,31]. It is also reported that ReO_x NPs contain ammonium ion, which is probably a Brønsted acid site in the catalyst [22]. In addition to dehydration, the acid sites on ReO_x might catalyze C-O cleavage of SAN to GBL. Recently, Li et al. studied C-O cleavage of lignin model compounds over ReO_x catalysts and acidic sites on ReO_x were responsible for the cleavage of C-O bonds [32]. The control test without catalyst under the same conditions (250 °C, 1 h) yielded ester compounds (Figure 1a). Even though esterification occurred at 250 °C without catalyst, ReO_x NPs facilitated esterification, yielding the higher SA-DE/SA-ME ratio.

The time profile of the conversion of SA over ReO_x/C is shown in Figure 1b. In a half-hour at 250 °C, all SA were converted to SA-ME/DE or GBL. Over the course of the reaction up to 6 h, SA-ME disappeared, yielding more SA-DE, GBL, and THF. THF can be made by the further CTH of the synthesized GBL, evident by the formation of THF from GBL as a starting material (Figure 1e). The reaction between 6 and 12 h indicates that SA-DE was also transformed to GBL while the CTH rate of SA-DE seems slower compared to the rate of transformation of SA. This agrees with Figure 1c that shows that GBL was slowly produced from SA-DE as a starting material. To investigate if the slow conversion of SA-DE was not due to catalyst deactivation, the used catalyst after 6 h reaction was replaced with a new catalyst, followed by 6 h further reaction (6 h + 6 h in Figure 1b). The product composition of the 6 h + 6 h reaction was similar to the 12 h reaction without interruption, excluding the possibility of deactivation. A higher temperature was required to facilitate the conversion of SA-DE to GBL. At the elevated temperature of 270 °C, more GBL (50% yield) was produced from SA in 1 h. The 3 h reaction yielded 60% GBL and 9% THF, with 22% of remaining SA-DE. Most of the SA-DE were converted in 6 h and CTH of GBL also proceeded, making more THF (28% yield) and other C4 compounds, including 1,4-butanediol (1,4-BDO) and butyric acid (BTA). Unsupported ReO_x NPs successfully catalyzed simultaneous CTH and dehydration of SA, yielding GBL and THF.

Isopropanol offered hydrogen for CTH, producing acetone as a co-product. The amount of the produced acetone after 250 °C/1 h reaction (5.5 mmol) was much higher than the theoretically required amount of H_2 (0.9 mmol) to produce 0.43 mmol of GBL and 0.02 mmol of THF. This indicates independent dehydrogenation of isopropanol over ReO_x NPs and the possibility of the involvement of the produced H_2 from isopropanol in the conversion of SA to GBL through direct dehydrogenation. To test this possibility, direct hydrogenation of SA was tested in dioxane with 15 bar of H_2, which is approximately 39 mmol H_2, calculated using the ideal gas law (Figure 1f). After 1 h at 250 °C, the amount of the synthesized GBL (16% yield) was much lower than that in the reaction with isopropanol as a reductant (43% yield). This demonstrates that the major pathway of the formation of GBL from SA is CTH reaction. In the presence of both isopropanol and molecular H_2, a higher amount of GBL (55% yield) was gained through both CTH and direct hydrogenation. The reaction under H_2 produced more unidentified products and showed lower mass recovery than the reaction in isopropanol without H_2 gas. This might be because unexpected side reactions occurred under H_2 atmosphere.

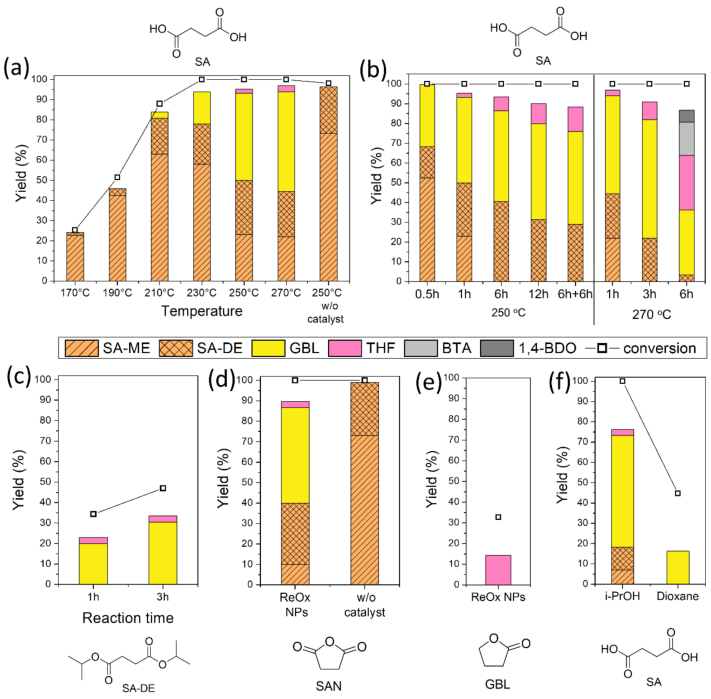


Figure 1. Conversion of succinic acid (SA), succinic anhydride (SAN), succinic acid diisopropyl ester

(SA-DE), and γ-butyrolactone (GBL) over ReO_x/C in isopropanol. (**a**–**e**) Reaction conditions: batch reaction, ReO_x NPs (10 mg, 4 mol% Re relative to substrate), substrate (1 mmol), *i*-PrOH (10 mL), and N_2 (15 bar); (**f**) H_2 (15 bar) and solvent (10 mL). Conversion and yield are calculated by ^{1}H NMR and GC-FID.

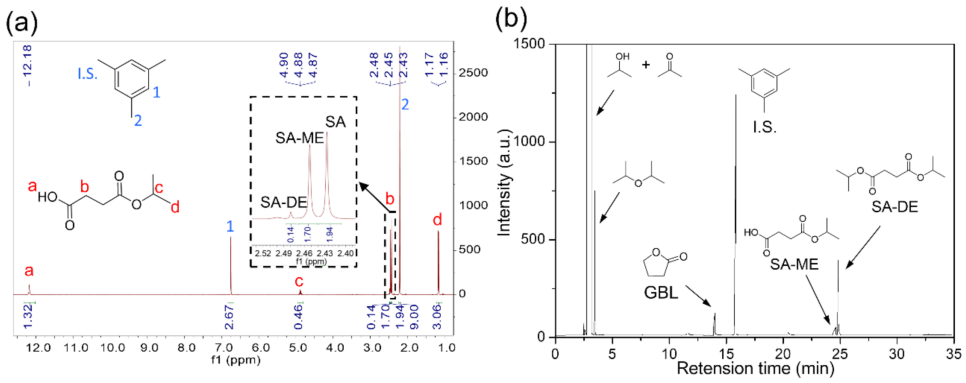
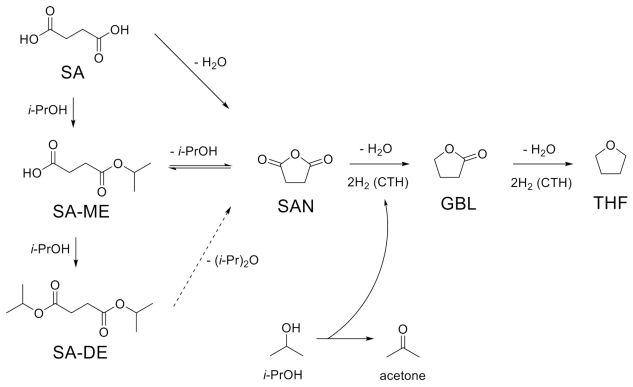


Figure 2. Product analysis: (**a**) NMR spectra of the reaction mixture of 190 °C and 1 h in Figure 1a. (**b**) GC spectra of the reaction mixture of 250 °C and 1 h in Figure 1a.



Scheme 1. Possible reaction pathway for the conversion of SA.

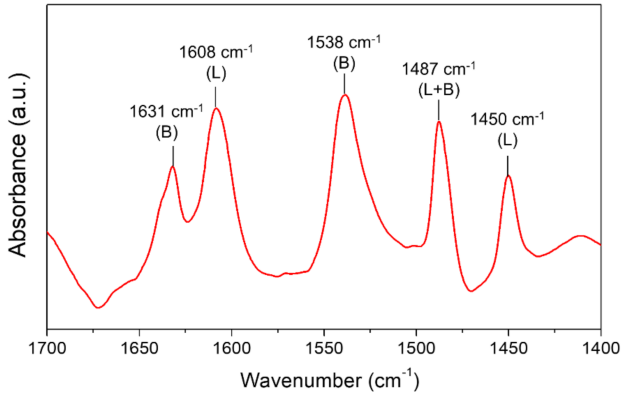


Figure 3. FT-IR spectra of pyridine absorbed on ReO_x NPs after pyridine absorption and desorption of physisorbed pyridine. L: Lewis bonded pyridine. B: Brønsted bonded pyridine.

3.2. Conversion of Maleic Acid (MA)

MA is another versatile 1,4-dicarboxylic acid because it includes an unsaturated bond. Figure 4 shows the conversion of MA with ReO_x NPs in isopropanol at different reaction temperatures. At all tested temperatures from 170 °C to 270 °C, esterification over ReO_x NPs converted MA to maleic

acid monoisopropyl ester (MA-ME) or maleic acid diisopropyl ester (MA-DE). Under the reaction conditions, MA and its esters were partially isomerized to fumaric acid (FA) and its esters (FA-ME and FA-DE). The resulting double bond compounds including MA, FA, and their esters were hydrogenated to SA, SA-ME, or SA-DE through CTH reaction with isopropanol as a hydrogen donor. At 170 °C, 13% yield of SA and its esters was obtained after 3 h reaction. At the elevated temperature of 250 °C, SA, SA-ME, and SA-DE are the major products, with a combined yield of 69% in 3 h. Similarly, CTH of MA to SA with noble metal catalysts and formic acid as a reductant was recently reported [33]. While CTH of C-C double bonds occurred without a catalyst, ReO_x NPs facilitated the CTH reaction and achieved a higher yield of C-C single bond compounds. Further conversion of SA and SA-ME/DE to GBL, as discussed in the previous section, produced GBL with yields of 15% and 29% at 250 °C and 270 °C, respectively. Moreover, 43% yield of GBL and 5% yield of THF were gained in the 6 h reaction at 270 °C.

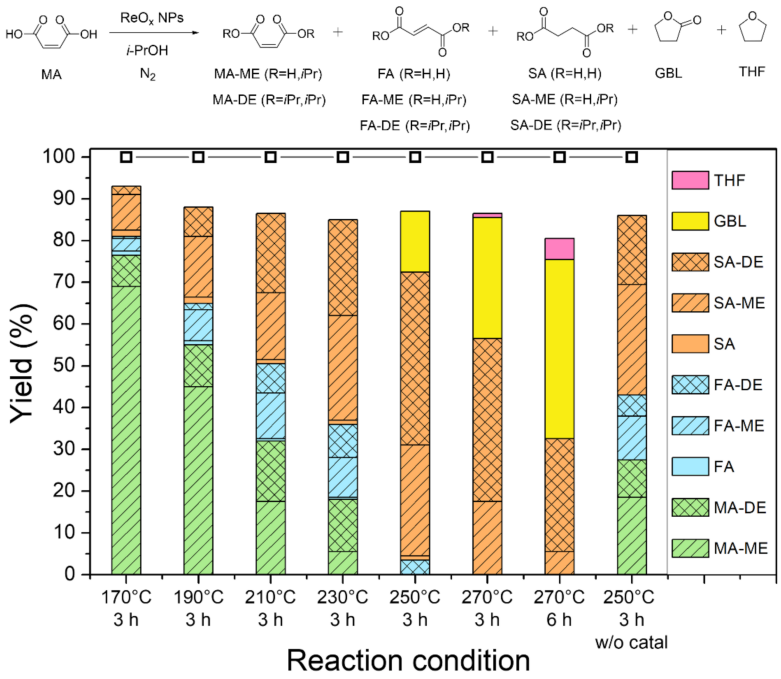


Figure 4. Conversion of maleic acid (MA) over ReO_x NPs in isopropanol: Reaction conditions: batch reaction, ReO_x NPs (10 mg, 4 mol% Re relative to substrate), MA (1 mmol), *i*-PrOH (10 mL), and N_2 (15 bar). Conversion and yield are calculated by ^{1}H NMR and GC-FID.

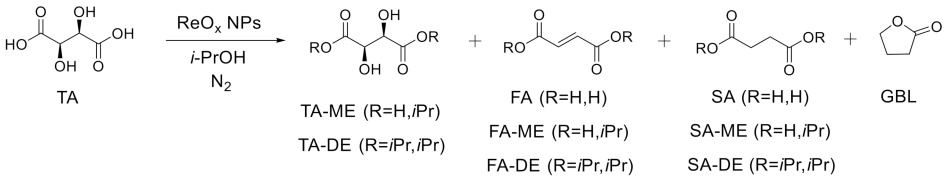
3.3. Conversion of Tartaric Acid (TA)

Unsupported ReO_x NPs and isopropanol directly convert SA and MA into GBL and THF. We previously demonstrated that the ReO_x NPs efficiently catalyzed the DODH reaction of glycerol with secondary alcohol as a reductant at 170 °C [22]. The possibility that DODH, combined with CTH and dehydration/dealcoholization, converts TA to GBL or THF in one step was investigated. First, transformation of TA to FA and its esters occurred on ReO_x through DODH and esterification at 170 and 210 °C (entry 1 and 2 in Table 1). The presence of TA-ME/DE in the products indicates that esterification of TA can take place before DODH occurs. However, DODH of TA can proceed first, making FA (4% yield in entry 1). MA and its esters were not detected, indicating that *trans*-alkene is the more favored DODH product from (*2R,3R*)-tartaric acid. It was reported that MTO-catalyzed DODH converted (*R,R*)-1,2-diphenyl-1,2-ethanediol to *trans*-stilbene while *cis*-stilbene was formed from (*R,S*)-1,2-diphenyl-1,2-ethanediol [34]. The high selectivity of FA and its ester from TA agrees with previous reports. Rhenium-catalyzed DODH produced high yields (> 85%) of FA or its ester from TA or its ester in the presence of various reductants including alcohol [19,35,36], metal [37], H_2 [38],

and triphenylphosphine [39]. Similarly, DODH has been employed to convert C6 sugar acids and their derivatives to valuable bio-based products [35,40–43].

At the reaction temperature above 250 °C, CTH reaction of C-C double bonds also proceeded as well as DODH, making SA and its esters (entry 3–5 in Table 1). In addition to the saturated products, GBL was also formed by simultaneous CTH and dehydration/dealcoholization, with a yield of 18% and 20% at 250 and 270 °C, respectively. In order to achieve a higher yield of GBL, the reaction was performed at 290 °C. After 12 h reaction, 34% yield of GBL was produced from tartaric acid and 18 h reaction produced more GBL, with a yield of 43%. Over the course of the reaction from tartaric acid, only a small amount of THF was formed (entry 5 and 6). A control experiment without catalyst showed small conversion, demonstrating that the conversion of TA was indeed catalyzed by ReO_x NPs (entry 7). The time profile of the TA conversion over ReO_x NPs at 290 °C is shown in Figure 5. Before the temperature reached 290 °C, all TA was already converted to TA-ME/DE or FA and its esters. The resulting FA and its esters were transformed to SA and its esters in 6 h. Over the course of 18 h, GBL was slowly produced from SA and its esters and 43% yield of GBL was attained. The high reaction temperature of 290 °C led to many side reactions and byproducts, including BTA and isopropyl branched GBL and succinate.

Table 1. Conversion of tartaric acid over ReO_x NPs [1].



Entry	Temp. (°C)	Time (h)	Conv. [2] (%)	Products/% Yield [2]					
				TA-ME,DE	FA and FA-ME,DE	SA and SA-ME	SA-DE	GBL	THF
1	170	12	100	28	65	0	0	0	0
2	210	12	100	13	75	1	2	0	0
3	250	12	100	0	0	30	17	18	0
4	270	12	100	0	0	18	20	23	0
5	290	12	100	0	0	10	6	34	2
6	290	18	100	0	0	0	1.5	43	1
7 [3]	250	12	100	92	4	0	2	0	0

[1] Reaction conditions: batch reaction, ReO_x NPs (10 mg, 4 mol% Re relative to substrate), TA (150 mg, 1 mmol), *i*-PrOH (10 mL), N_2 (15 bar). [2] Conversion and yield are calculated by ^{1}H NMR and GC-FID. [3] Without catalyst.

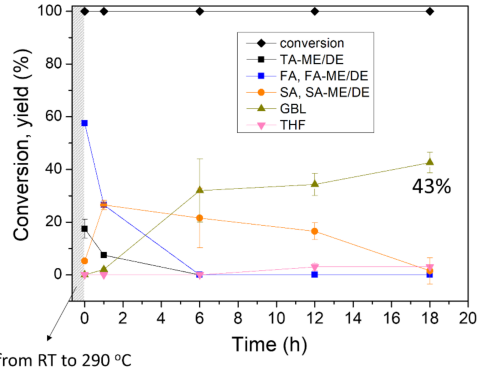
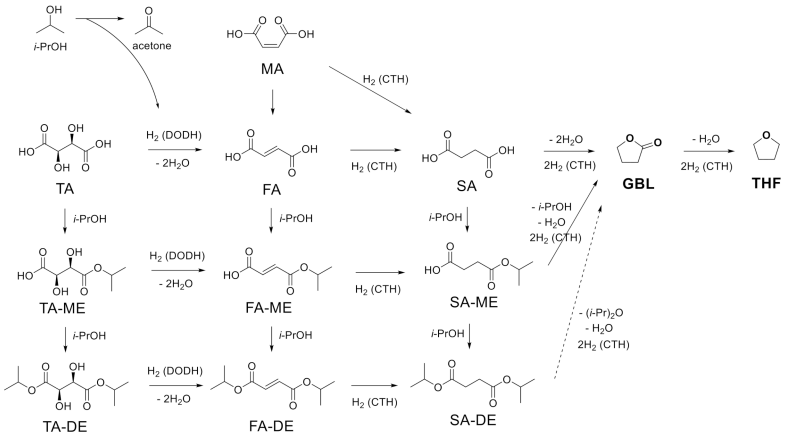


Figure 5. Reaction profile of the conversion of tartaric acid (TA) at 290 °C. Reaction conditions: batch reaction, ReO_x NPs (10 mg, 4 mol% Re relative to substrate), TA (1 mmol), *i*-PrOH (10 mL), and N_2 (15 bar). Conversion and yield are calculated by ^{1}H NMR and GC-FID.

3.4. Reaction Pathway

Based on the results of the conversion of SA, MA, and TA with unsupported ReO_x NPs, the possible reaction scheme is illustrated in Scheme 2. In isopropanol, the carboxylic acid group in TA is esterified, making TA-ME or TA-DE. TA and its esters are converted to FA and its esters through DODH, removing hydroxyl groups and making a *trans*-double bond. Hydrogen is provided from isopropanol for DODH reaction. This step produces acetone as a byproduct. CTH reaction over ReO_x in isopropanol saturates the resulting double bonds in FA, FA-ME, and FA-DE to SA, SA-ME, and SA-DE, respectively. SA undergoes intramolecular dehydration and CTH, affording GBL. Dealcoholization and CTH also produce GBL from SA-ME/DE. Further CTH of GBL yields THF. MA, another starting material, is isomerized to FA. Both MA and FA can be hydrogenated to SA and the resulting SA and SA-ME/DE follow the same pathway, giving GBL and THF.



Scheme 2. Possible reaction pathway for the conversion of succinic acid (SA), maleic acid (MA), and tartaric acid (TA).

4. Conclusions

In this study, valuable C4 chemicals including GBL and THF were synthesized from SA, MA, and TA through ReO_x-catalyzed DODH, CTH, and cyclization reactions. Isopropanol provided hydrogen for both DODH and CTH reactions without needing the addition of H_2 gas. GBL was produced from SA at a temperature above 200 °C with a possible intermediate of SAN. Intramolecular dehydration of SA or dealcoholization of SA-ME/DE was catalyzed by acidic sites on ReO_x, evident by the pyridine probe FT-IR result. CTH-assisted C-O bond cleavage proceeded with ReO_x NPs, producing GBL from SAN. Further CTH of GBL yielded THF. The highest yield of GBL from SA was 60%, with 9% yield of THF at 270 °C. SA and its esters can be prepared from MA by CTH of C-C double bond and from TA by DODH-CTH of a diol. Under the optimized conditions, ReO_x NPs afforded 43% yield of GBL from TA with isopropanol as a hydrogen donor in one step.

Author Contributions: Designed and conducted experiments, analyzed data, and wrote manuscript, J.H.J.; designed experiments, interpreted data/results, and edited manuscript, M.M.A.-O. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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