RESEARCH ARTICLE

One-pot Production of Succinic Acid from Tartaric Acid in Water by Supported Rhenium Catalyst

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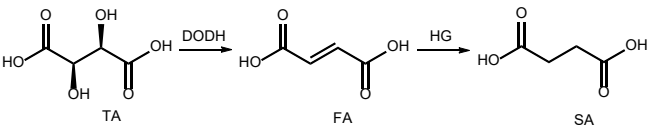
Abstract: The formation of dicarboxylic acid from biomass waste is an important topic for the sustainable production of polymers. Rhenium catalyzed deoxydehydration (DODH) of aldaric acid to enedioic acid followed by hydrogenation (HG) is one of the possible routes to form carboxylic acids. However, reliance on organic solvents and noble metals poses a risk to the sustainability of the process. Herein, we demonstrated for the first time the conversion of tartaric acid (TA) to succinic acid (SA) in water in one-pot reaction using heterogeneous ReO_x/activated carbon (ReO_x/AC) without the addition of noble metals, in which ReO_x/AC catalyzes both DODH and HG. At TA conversion >99%, SA yield of 76% is obtained. TA concentrations as high as 10 wt.% could be employed and unprecedentedly high turnover number (TON, 144) and SA productivity (0.24 $g_{SA} \cdot g_{catalyst}^{-1} \cdot h^{-1}$) are obtained. The use of water facilitates the HG of fumaric acid intermediate, showing a 17-fold faster HG step compared to conventional dioxane. The catalyst was reused over four reaction cycles.

In recent years, the field of biomass valorization has gained significant attention as researchers seek sustainable alternatives to petroleum-based chemicals.[1,2] However, the high content of oxygen of biomass-derived molecules starkly contrasts with the oxygen-poor nature of petroleum-based chemicals, making it unsuitable for direct integration into existing petrochemical processes. Consequently, the reduction of oxygen content in biomass-derived compounds emerges as a critical step. Among the various strategies developed to address this challenge, the deoxydehydration (DODH) reaction has gained significant attention.[3-5] The DODH reaction, which converts vicinal diols into olefins, has been extensively studied using various transition metal catalysts, with Re-based systems showing promise.[6-10] The olefins obtained by DODH reaction can be reduced to saturated carbon bonds by means of hydrogenation (HG), often carried out by the aid of a noble metal; Scheme 1 shows DODH/HG reaction from tartaric acid (TA) to succinic acid (SA) via fumaric acid (FA). A variety of catalytic systems comprising of combination of Re and another metal (Pd, Pt, Ir, Au, Ni) supported on different materials have been reported for DODH/HG tandem reaction of polyols and aldaric acids into saturated diols and dicarboxylic acids.[11-15] Amongst aldaric acids, tartaric acid (TA) and mucic acid are attractive biomass-derived substrates because of the usefulness of their DODH/HG products in the polymer synthesis: SA and adipic acid. Production of these acids is still reliant on fossil fuel,[16,17] but recently methods for catalytic production of organic acid from biomass-derived platform are increasing.[18-20] As a starting material, TA is of particular interest because it is a naturally occurring acid present as a major constituent of grape lees (a by-product of the winemaking industry), therefore being readily available from biomass waste after only simple purification steps.[21,22]



Scheme 1. DODH/HG tandem reaction of tartaric acid (TA) to succinic acid (SA) via fumaric acid (FA).

Conversion of TA to SA by DODH/HG tandem reactions was performed by several groups. Fu et al. employed a MoO_x/carbon black (CB) catalyst in a system comprising TA, acetic acid, HBr and H_2.[23] The final yield of SA of this one-step process was 87% at 170°C in 24 h. Li et al. demonstrated that both homogeneous and supported Re were active for DODH of TA to maleic acid (MMA) using 3-pentanol as both a solvent and a reducing agent, and the following hydrogenation into SA was performed in a separate step with H_2 and Pt/C catalyst upon isolation of MMA intermediate; final yield of SA was 95%.[24] Unsupported ReO_x nanoparticles were moderately active for DODH/HG of TA to SA (and their mono- and di-esters) in isopropyl alcohol only at temperature higher than 250°C.[25] As the examples listed above, most DODH/HG systems rely on organic solvents and noble metals, which significantly limits their environmental sustainability.

In particular, dioxane and methanol are amongst the most used solvents for DODH reaction, and although they may offer an easier product recovery, their high toxicity is a matter of concern.[26] The use of water is therefore desirable, because it improves the overall safety of the process and allows to work with concentrated substrate solutions. Larson et al. successfully achieved the conversion of glucarodilactone to adipic acid in water by using a homogeneous $KReO_4$ catalyst stabilized by 4-dimethylaminopyridine in the presence of Pd/C and activated carbon.[27] Hočevar et al. showed that Re/C, upon reduction, can perform DODH and HG in one-pot without noble metals in methanol, using either hydrogen or methanol as reducing agents.[28] These advancements represent a significant step forward in DODH/HG reaction as they showed that dependency on organic solvent or noble metal can be circumvented. However, to the best of our knowledge, a system without using both characteristics has not yet been demonstrated. In this work, we aim to demonstrate that heterogeneous ReO_x supported on activated carbon (ReO_x/AC) catalyst can perform efficiently DODH/HG tandem reaction of TA to SA in water using hydrogen as a reducing agent without the addition of second noble metals. Furthermore, the catalyst is shown to be active with a high concentration of TA and the reaction is scalable up to the gram level.

Several heterogeneous ReO_x catalysts with supports of different nature were reacted with an aqueous solution of TA and H_2 at 150°C for 15 h (Table 1). Amongst the tested catalysts ReO_x/AC exhibited the best performance with >99% conversion and 57% yield of SA under the screening reaction conditions. Re supported on carbon black (ReO_x/CB) led to 40% conversion and only 10% of SA yield. Re supported on SiO_2, Al_2O_3 and CeO_2 did not form SA. ReO_x/TiO_2 formed 29% of SA and 24% of malic acid (MA), showing low selectivity of one product. Homogeneous catalysts $MeReO_3$ and NH_4ReO_4 exhibited poor performances, with low conversions and SA yields. As other products, only FA and MA were detected. Neither γ-butyrolactone nor 1,4-butanediol were detected in any case, showing that hydrogenation of SA did not occur under these reaction conditions. In the absence of H_2, ReO_x/AC only showed negligible activity for DODH reaction, indicating that H_2 is necessary for activating the Re species to carry out DODH. When the AC support alone was reacted, no DODH products were detected.

Given the superior performance of ReO_x/AC, we selected this catalyst for further investigations. In the temperature range of 125-175°C the yield of SA did not significantly change (55-59%), and TA conversion was always >99% (Figure S1). Decrease of SA yield to 26% was observed when the temperature was lowered to 100 °C, but TA conversion was still maintained at >99% while FA was detected with 18% yield. A drastic drop of conversion to 51% and no SA yield was observed at 80°C. The catalyst was active in the 0.5 – 3 MPa pressure range; in all cases SA was obtained as the only product with full conversion of TA. We chose to perform the reaction at 1 MPa to operate well above the vapor pressure of water at 150°C (Figure S2). When the catalyst amount varied from 25 to 100 mg, TA conversion was in all cases >99% but SA yield linearly decreased from 70% to 25% (Figure 1a). No other products other than SA were detected in NMR analyses (Figures S3 and S4). To see if some products were strongly adsorbed on the catalyst, the catalyst was thoroughly washed with a known amount of water. From the washed solution, SA was only detected, and the yield increased from 57 to 69% (Figure S5). This pointed out that relevant adsorption phenomena were in play. From the Langmuir adsorption isotherm, the value of Langmuir constants (K_L) and maximum substrate adsorption (q_m) were calculated and then the amount of adsorbed product was estimated (Figure S6, Table S1). When the estimated amount of adsorbed SA was added to the SA yield in the experiment shown in Figure 1a, the carbon balance exceeded 90% in all cases, showing that indeed adsorption of SA accounts for most of the carbon loss. Accordingly, operating the reaction with a higher substrate-to-catalyst ratio (S/C) could be beneficial for reducing the fraction of product lost by adsorption on catalyst.

Table 1. Screening of catalysts for DODH/HG of TA.[a]

Entry	Catalyst	Re loading[b] %	BET S.A. m^2g^{-1}	TA Conv. %	SA yield %	FA yield %	MA yield %
1	ReO_x/AC	4.4	1043	>99	57	0	0
2	ReO_x/CB	3.9	1130	40	10	0	1
3	ReO_x/SiO_2	3.3	262	<1	0	0	0
4	ReO_x/Al_2O_3	4.0	197	75	0	<1	0
5	ReO_x/CeO_2	4.1	85	99	0	1	<1
6	ReO_x/TiO_2	3.6	108	53	29	0	24
7	$MeReO_3$	-	-	23	6	9	1
8	NH_4ReO_4	-	-	2	<1	<1	<1
9[c]	ReO_x/AC	4.4	1043	34	0	2	0
10	AC	-	-	26	0	0	0

[a] Reaction conditions: 3 mL of 0.65 wt% TA aq. solution, 50 mg cat, 150°C, H_2 1 MPa, 15 h. [b] Re loading was measured by means of ICP analysis. [c] 1 MPa of Ar was used instead of H_2.

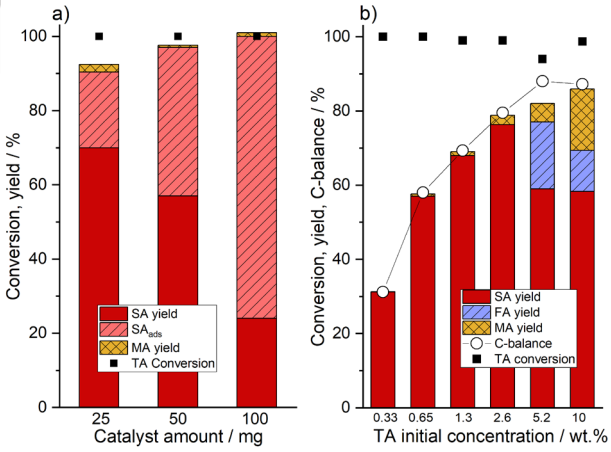


Figure 1. a) Catalyst loading effect on DODH/HG reaction. The pink striped bar represents the calculated SA adsorbed on the catalyst by using Langmuir equation. Reaction conditions: 0.65 wt% TA aq. solution, various amount of catalyst,150°C, H_2 1 MPa, 15 h. b) Effect of TA initial concentration on the DODH/HG products distribution. Reaction conditions: 3 mL of TA aq. solutions at different concentrations, 50 mg cat, 150°C (175°C for the reaction with TA 10 wt%), H_2 1 MPa, 15 h.

To verify this, the initial concentration of TA was changed from 0.33 wt% to 10 wt% while keeping the catalyst amount constant at 50 mg (Figure 1b, Table S2). Other conditions were kept the same, with the only exception of the reaction with 10 wt%

where the temperature was set to 175°C to increase the solubility of FA and avoid its precipitation during the reaction. As anticipated, the carbon balance of the reaction steadily increased as the S/C increased, confirming that the observed carbon loss was caused by product adsorption. Up to 2.6 wt%, SA yield steadily increased until a maximum value of 76%; FA was not detected and MA yield only reached 2.5%. When TA concentration was set to 5.2 wt% and 10 wt%, SA yield decreased to 59%; higher yields of FA and MA were also observed at these concentrations. Despite the decrease in SA yield at higher concentrations, TON and SA productivity greatly benefits from the increased substrate concentrations. At 10 wt% TON of 144 was achieved and SA productivity ($g_{SA} \cdot g_{cat}^{-1} \cdot h^{-1}$) was calculated to be about 0.24 h^{-1} in a large-scale reaction (Table S2, #7). The performances of this catalytic system were compared with previously reported works for the DODH/HG tandem reaction of aldaric acid with solid catalysts (Table S3). Generally, the lower concentration of reactants and the lower substrate-to-metal ratio (S/M) used in other systems lead to TON and SA productivity values remarkedly inferior to the ones obtained in this work. In particular, the use of water as solvent is a key element to increasing the concentration of the free tartaric acid. When the reaction scale was increased 10 times from 3 mL to 30 mL scale, no substantial changes in performance were observed, pointing out easy scalability up to the gram scale of this system (Figure S7, Table S2 #6-7).

Time course of the reaction was followed to understand the reaction kinetics and pathways (Figure 2). TA is rapidly consumed within 4 h and FA is the main product formed within 2 h. As the reaction proceeds further, FA content starts to decrease until total consumption and SA gradually forms. After 15 h of reaction SA is the main product with 70% of the yield. MA is steadily formed during the reaction, reaching a final yield of 2.5%. Subsequently, the reaction pathway was investigated. MMA is not observed, leaving MA and FA as the two intermediate candidates for SA formation. When hydrogenation of FA and MA was performed, SA was formed from FA but not from MA, clearly indicating FA as the intermediate for SA formation (Figure S8a). MA is a by-product of reaction; in another control experiment it is shown that MA is only observed starting from TA and FA but was not formed from SA (Figure S8b). As the yield of MA is higher when the reaction is performed from FA directly than from TA, FA was indicated as the precursor to MA. MA can be formed by hydration of C=C double bond of FA. Indeed, higher yields of MA are obtained when the initial TA concentrations are higher, which causes a decrease of pH to facilitate hydration of C=C double bonds. In summary, TA undergoes DODH to form FA that is hydrogenated to SA. A small portion of FA goes through hydration to form MA (Scheme S1).

The time course data were fitted using the following pseudo-first order kinetics

$$d[TA]/dt = -k_1[TA] - k_4[TA]$$

$$d[FA]/dt = k_1[TA] - k_2[FA] - k_3[FA] - k_5[FA]$$

$$d[SA]/dt = k_2[FA] - k_6[SA]$$

$$d[MA]/dt = k_3[FA]$$

and the kinetic constants for each step were calculated (Scheme 2, Table 2). Values of k_1 (TA→FA), k_2 (FA→SA) and k_3 (FA→MA) were determined to be 0.60, 0.36 and 0.015 h^{-1}, respectively. Successively, the kinetics of the reaction in dioxane as solvent were measured as a comparison, since organic solvents are typically preferred to water for the DODH reaction (Figure 2b). The k_1 and k_2 were estimated to be 1.8 and 0.021 h^{-1}, showing that while the DODH step benefits from using dioxane, as already observed in previous works,[29,30] HG step was significantly slower with a k_1/k_2 ratio of 85.

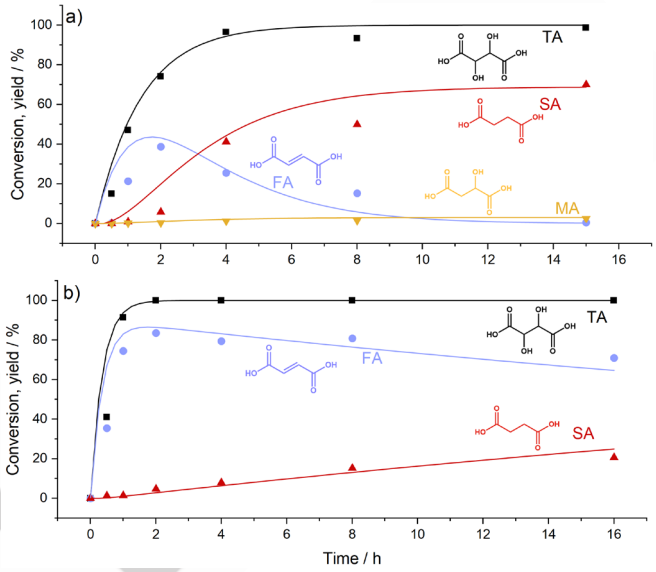
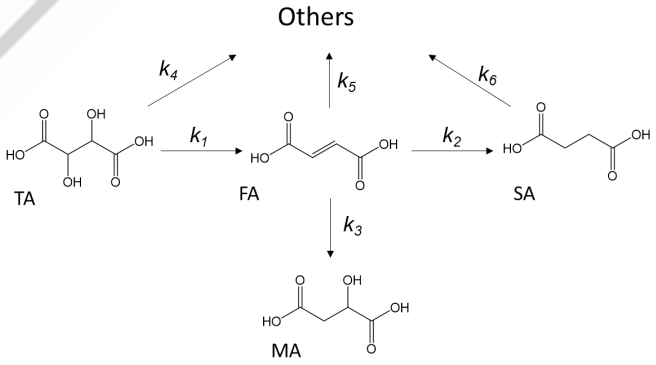


Figure 2. Time course of DODH/HG tandem reaction with ReO_x/AC in a) water and b) dioxane as solvents. Reaction conditions: 3 mL of 0.65 wt% TA aq. solution, 20 mg cat, 150°C, H_2 1 MPa. Experimental data are represented by symbols (▲, ■ and ●) and modeled kinetics are represented by lines.



Scheme 2. Kinetic model of DODH/HG of TA to SA with ReO_x/AC in the presence of hydrogen.

Table 2. Kinetic constant of TA DODH/HG calculated by modelled kinetics.

		Kinetic constant / h^{-1}					
Entry	Solvent	k_1	k_2	k_3	k_4	k_5	k_6
1	water	0.60	0.36	0.015	0.060	0.060	0.030
2	dioxane	1.8	0.021	0	0.21	0	0

The catalyst was characterized by a variety of techniques. ReO_x/AC catalyst particles exhibit rough surface and irregular shape, with dimensions comprised between 10 µm and 100 µm (Figure S9a and b). XRD analysis of ReO_x/AC did not show any diffraction peaks attributable to crystalline phase, indicating that Re particles were finely dispersed (Figure S10).[31] Indeed, STEM

analysis showed that Re was highly dispersed on the carbon surface (Figure S11). Very small particles in the range 0.1-0.4 nm were predominantly observed, suggesting that Re was mainly atomically dispersed (Figures 3 and S12, Table 3). The largest particles detected were about 1 nm in diameter. *D*-spacing of some particles were measured to be 0.19 and 0.24 nm, corresponding to Re_2O_7 and ReO_2, respectively (Figure S13).[32] XPS analysis showed that almost all Re is present in high oxidation states, presumably Re^{VII}, with a main peak of Re $4f_{7/2}$ centered at 45.5 eV and a smaller peak centered at 43.0 eV indicates the presence of more reduced Re^{IV} (Figure S14a).[13,28,29]

Table 3. Diameter distribution of Re particles taken from STEM measurements.

		Diameter distribution / %				
Entry	Catalyst	0.1-0.4 nm	0.5-0.8 nm	0.9-1.2 nm	1.3-1.6 nm	1.6-2.0 nm
1	Fresh	92	3	5	-	-
2	Used	54	11	14	14	7

In order to clarify the Re species involved in the DODH/HG catalysis, we measured the oxidation state of Re under different conditions and tested their activity for DODH and HG. The reduced catalyst was loaded in the reactor and in the XPS chamber without exposing it to air to avoid oxidation. The fresh catalyst containing Re^{VII} was active for both DODH and HG. In a control experiment, a reduced ReO_x/AC constituted of mainly Re^{II}/Re^{III} species (41.5 eV) and minor Re^{IV} species (Figure S14b) was shown to be able to convert FA to SA, but it failed to efficiently convert TA (Figure S15). When the catalyst was reduced under the reaction conditions (stirred in water under 1 MPa H_2 at 150°C for 4 h), the majority of Re was reduced to Re^{IV} (Figure S14c). Given the fact that the more reduced Re^{II}/Re^{III} are not formed under the reaction conditions, it is likely that Re^{IV} is responsible for both DODH and HG steps. These findings agree with the widely accepted DODH mechanism proceeding with Re^{VI}-Re^{IV} redox pairs (Scheme S3);[33,34] overreduction of Re clearly hinders the activity for DODH step, but it is active for HG. Although limited, use of monometallic Re as HG catalyst is known in literature.[35] In addition, examples of HG of C=C double bonds with Re were shown by Berke group with organo-Re^{I} complexes[36,37] and She et al. using a ReO_x/TiO_2 to selectively hydrogenate muconic acid into adipic acid.[38]

We observed a promotional effect of water for the formation of SA from TA. Reducing the catalyst in dioxane yielded nearly identical Re species to those observed in water (Figure S14d). This suggests that dioxane does not hinder the formation of DODH/HG active Re^{IV}. For this reason, it is plausible that the enhancement of HG rate comes from direct participation of water during the HG reaction. Indeed, water is known to stabilize reactive H* species into a more stable H_3O* intermediate with increasing mobility on the catalyst surface.[39] Dou et al. also observed an increased rate of HG of maleic acid to SA with H_2 and Pd/C thanks to direct participation of water by forming a stable H_3O* intermediate that halves the activation energy compared to the one obtained in dioxane.[40] Further investigations are needed to clarify the exact nature of Re for HG and how water participates in our system.

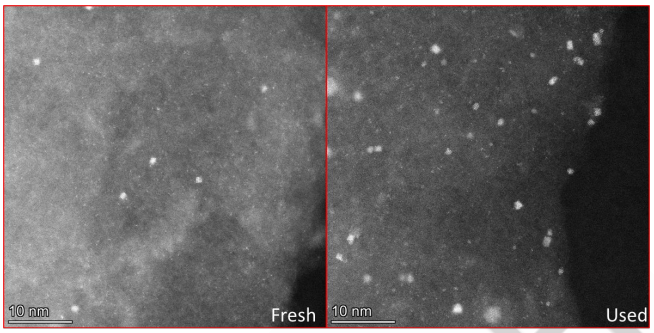


Figure 3. STEM image of fresh (left) and used (right) ReO_x/AC. Re particles are represented as white spots.

To assess catalyst recyclability, ReO_x/AC was reacted in four consecutive cycles (Figure 4a). TA conversion slowly decreased from an initial 95% to 81% at the end of the fourth cycle. SA yield decreased from 77% to 65%. FA yield increased after each reuse, reaching a final value of 7%. Additionally, to get a better insight into the real extent of deactivation we repeated the recycling test at a shorter reaction time, allowing to investigate the deactivation at a more kinetic relevant point of the reaction (Figure 4b). Under these conditions it was shown that the actual extent of deactivation was partially masked by the high conversion of previous test and showed that the initial activity decrease to 40% after 4 runs. Stability of heterogeneous Re catalyst during DODH processes is extensively studied in literature, with leaching, sintering and fouling indicated as the main deactivation causes.[41,42] Re leaching is a very complex phenomenon, because it is influenced by a combination of multiple factors such as solvent, support and type of diols. Hočevar et al. showed that on their Re/AC Re leached up to 14% after just one run and the catalyst activity decreased by 50% of its initial value after four catalytic runs.[28] Li et al. measured a total Re leaching of 51% and 40% of initial activity was lost at the end of the fifth cycle.[24] Abu-Omar group indicated fouling by carbon deposition as the main cause of deactivation of Ir-Re/C and Pt-Re/C.[13,15] On the other hand, Tomishige group reported that the main deactivation mechanisms on Re-Pd/CeO_4 was sintering of active Re single atoms into inactive Re clusters, stating that DODH was indeed very sensitive to the Re sites morphology.[43,44] To understand the cause of deactivation in our system, the spent catalyst and reaction liquor were investigated by several techniques. The catalyst morphology was not greatly affected, showing just some increase of the surface roughness, possibly caused by smaller particles aggregation (Figure S9c and d). XPS analysis revealed that Re at the end of the reaction is in high oxidation state, Re^{VII} and Re^{VI}, showing that permanent overreduction did not take place and these species might be again reduced to active Re^{IV} under reaction conditions (Figure S14e). This result indicates that Re, probably just by the action of the oxygen present in the atmosphere, is promptly re-oxidized to high oxidation state. TGA analysis on the spent catalyst showed an initial weight loss of 8% after the first reaction cycle; however no more substantial decrease was detected in the following cycles, with only a final 10% weight loss measured at the end of the last run, showing that

the major build-up of carbon happened during the first cycle (Figure S16). Thus, it is not expected to play a relevant role for deactivation after the second cycle. In addition, treating the used catalyst at 300°C failed to restore the original catalyst activity (Figure S17). From these results, we exclude that carbon deposition on the catalyst is the main cause of deactivation. ICP analysis of the reaction solution at the end of each cycle showed that some Re leached at a similar rate after each reaction; at the end of the last cycle the total Re leached content measured in the solution accounted for 8.5% of the Re in the fresh catalyst (Figure 4a). A hot-filtration experiment was performed to clarify if leached Re contributes to the catalysis (Figure S18). The reaction stops progressing after the catalyst was removed, demonstrating that homogeneous Re is not active under the current reaction conditions. The relatively low extent of leaching compared to the measured deactivation suggested that an additional deactivation mechanism could also play an important role. STEM analysis performed on the used catalyst revealed that size distribution of ReO_x particles after the 4th cycle of reaction visibly broadened, and most of the original small particles (0.1-0.4 nm) sintered to form a broader distribution spanning in the 0.1-2.0 nm range (Figures 3 and S19, Table 3). However, particles bigger than 2.5 nm were not observed. The original distribution of particles 0.1-0.4 nm decreased from 92% to 54% (Table 3) showing to be the most dramatic change observed on the catalyst. Sintering was probably caused by the action of hydrogen as the sintered particles are similar in size to the particles found in the reduced catalyst used for control experiments (Figure S20). Aggregates of Re particles have been reported to be less active compared to single Re sites.[43,44] We can then conclude that combination of leaching and sintering played a major role in the deactivation of the catalyst.

In summary, we found that SA can be effectively obtained from TA in a one-pot reaction in water with ReO_x/AC in the presence of hydrogen. The catalysis is of heterogeneous nature and has high TON and SA productivity. Efforts to understand the effect of solvent and to reduce the catalyst deactivation are undergoing.

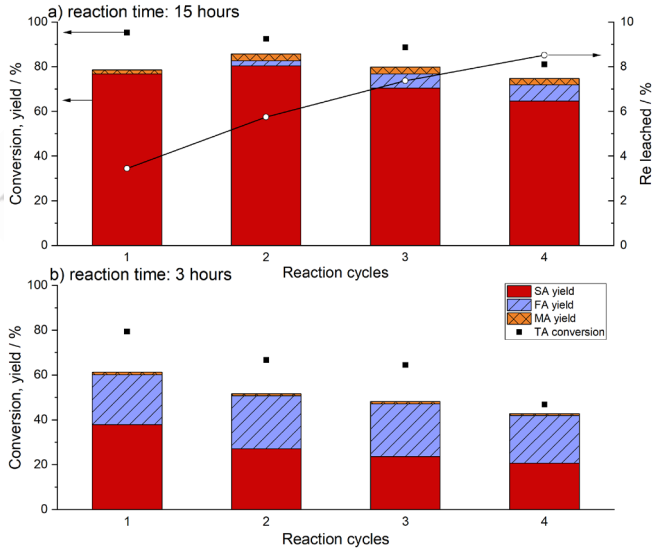


Figure 4. Recycling test of ReO_x/AC during DODH/HG reaction of TA performed at different reaction time. The catalyst has been recovered by filtration and dried in a vacuum oven for 6 h at 100°C before each re-use. Reaction conditions: 3 mL of 2.6 wt% TA aq. solution, 50 mg cat, 150°C, H_2 1 MPa; reaction time: a) 15 h, b) 3 h.

Supporting Information

Data relating to the materials and methods, adsorption, kinetic studies and characterization of catalysts.

Acknowledgements

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Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings in this study are available from the corresponding authors upon reasonable request.

Keywords: Deoxydehydration • Hydrogenation • Rhenium catalyst • Succinic acid • Tartaric acid

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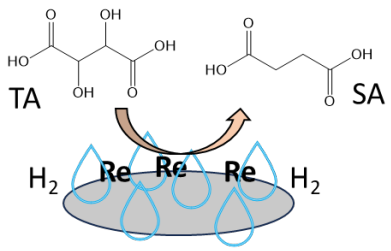

Sustainable production of succinic acid (SA) from tartaric acid (TA) is achieved by ReO_x/AC catalyst in water. High TON and SA productivity are obtained, and the reaction is scalable up to the gram-scale. Water promotes the hydrogenation rate of more than one order of magnitude compared to organic solvent (dioxane). *In situ* generated Re^{IV} is presumed to be an active species. Re sintering and leaching are possible causes of deactivation.