

Selective Hydrodeoxygenation of Tartaric Acid to Succinic Acid

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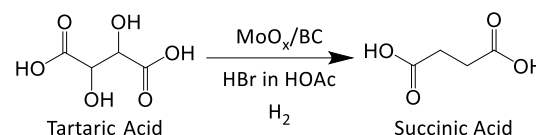
Highlights

- A one-step catalytic process for producing succinic acid from tartaric acid is developed
- Succinic acid is obtained with yield as high as 87%
- Strong synergy between MoO_x/black carbon and HBr in C-O bond cleavage is identified
- Structure-catalytic performance correlations over MoO_x/BC catalyst are established

1. Introduction

The increase of atmospheric greenhouse gas emissions is driving the development of biomass-based technologies for the sustainable production of renewable chemicals and fuels.¹ Succinic acid (SA), a four-carbon dicarboxylic acid (C₄H₆O₄), is recognized by the Department of Energy (DOE) as one of the top biomass-derived platform chemicals.² Its main applications include synthesis of valuable C₄ commodity chemicals (tetrahydrofuran, 1,4-butanediol and γ -butyrolactone) and biodegradable polymers.² Fermentation of glucose has been proposed as a renewable alternative, yet low productivity is a drawback.³

We developed a novel one-step catalytic process for high yield synthesis of SA from biomass-derived tartaric acid (TA) (**Scheme 1**). TA is naturally produced in the waste streams of winery industry.⁴ A liquid-phase system under hydrogen atmosphere comprised of a molybdenum oxide catalyst supported on carbon black (MoO_x/BC) and hydrobromic acid (HBr) in acetic acid as a solvent is effective for selective cleavage of C-O bonds of TA and selective hydrogenation of C=C present in reactive intermediates. The roles of MoO_x/BC and HBr are identified and the importance of Mo oxidation state is elucidated.



Scheme 1. Succinic acid production from tartaric acid via hydrodeoxygenation (HDO).

2. Methods

Molybdenum trioxide (MoO₃) was synthesized by calcining ammonium molybdate tetrahydrate under air flow (100 sccm) at 500 °C for 3 h. Impregnation was performed in 25 mL deionized water with 1.5 g MoO₃ and 3.5 carbon black (XC72). After 2 h of stirring, water was removed with a rotary evaporator and the remaining solids were dried in oven at 120 °C overnight. Before each experiment, MoO_x/BC was activated in flowing hydrogen at 50 sccm and 500 °C for 0.5 h. All experiments were conducted in a 50 mL Parr reactor. Typically, 0.2 M TA, 0.1 M (or 0.01 M) HBr and 306 mg MoO_x/BC were mixed in acetic acid. The reactor was pressurized with hydrogen (4.5, 13, or 37 bar) and heated to the predetermined temperature (120, 140, 170, or 200 °C). After reaction, the reactor was quenched in an ice bath and solid catalysts were separated. Liquid product samples were analyzed with an Agilent 1200 Series HPLC equipped with a refractive index detector. Catalyst characterization was performed using X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). Multiple substrates along with trajectories were used to develop a reaction network.

3. Results and discussion

We found that HDO of TA to SA is accomplished in 0.1 M HBr and partially reduced MoO_x/BC with 63% yield at 170 °C in 5 h and 87% yield in 24 h. Time dependent experiments reveal that reaction

proceeds via three key steps: C-O bond cleavage in TA and formation of esters of TA, elimination of hydroxyl group from the malic acid (MA) or acetate group from 2-acetoxysuccinic acid (EMA) to fumaric acid (FA), and FA hydrogenation to SA. To unravel the roles of MoO_x/BC and HBr, controlled experiments (without and with only HBr or MoO_x/BC added) were conducted (Figure 1). The blank experiment with acetic acid solvent shows that the solvent participates in the esterification of two hydroxyl groups of TA and is inactive for cleaving the C-O bonds in TA. When either HBr or MoO_x/BC is added to the system, C-O bonds in TA cleave forming MA, EMA and FA. This suggests that HBr or MoO_x/BC alone is capable of catalyzing C-O bond cleavage of TA. However, the rate of C-O bond cleavage is slow. Notably, hydrogenation of FA to SA occurs only in the presence of MoO_x/BC. This is consistent with a metallic function of the partially reduced MoO_x reported previously⁵ and our XPS data showing metallic Mo and low-valent Mo^{+δ} (0 < δ < 4) on the surface of MoO_x/BC when the catalyst is reduced at 500 °C. HBr alone promotes undesired side reactions, forming pyruvic acid as a byproduct. Interestingly, when HBr and MoO_x/BC are combined, the yields of MA and subsequent products, especially SA, increase significantly with a concomitant decrease in TA and its esters. This indicates a strong synergy between HBr and MoO_x/BC in promoting HDO of TA. Experiments have been conducted starting with different substrates to verify the reaction network. Furthermore, catalyst optimization and active site determination have been conducted by performing systematic catalyst reduction studies and correlating catalyst properties obtained via XRD, XPS, and XAS with reactivity (not shown).

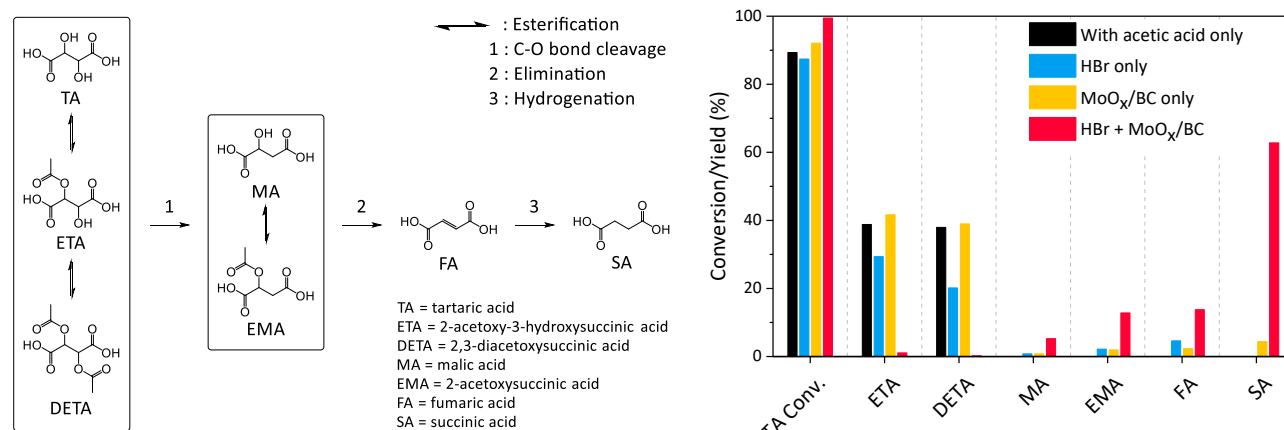


Figure 1. (Left) Proposed reaction network; (Right) Effect of HBr and MoO_x/BC on SA production. Reaction conditions: 0.2 M TA, 0.1 M HBr, 9 mL acetic acid, 306 mg MoO_x/BC, T = 170 °C, P_{H2} = 37 bar (initial pressure), and reaction time = 5 h.

4. Conclusions

An efficient one-step catalytic process for the hydrodeoxygenation of tartaric acid (TA) to succinic acid (SA) was developed using MoO_x/BC and HBr in acetic acid. The catalyst selectively reduces the hydroxyl groups of TA while impedes the reduction of carboxyl groups. Strong synergy between MoO_x/BC and HBr facilitates the formation of malic acid via C-O bond cleavage, whereas partially reduced MoO_x/BC catalyzes the hydrogenation of fumaric acid intermediate to SA. Catalyst characterization indicates that low-valent Mo^{+δ} (0 < δ < 4) and metallic Mo sites are active for hydrogenation.

References

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Keywords

Wine waste; Renewables; Succinic acid; Molybdenum oxide.