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Adipic Acid Production Catalyzed by a Combination of a Solid Acid and an Iodide Salt from Biomass-Derived Tetrahydrofuran-2,5-dicarboxylic Acid

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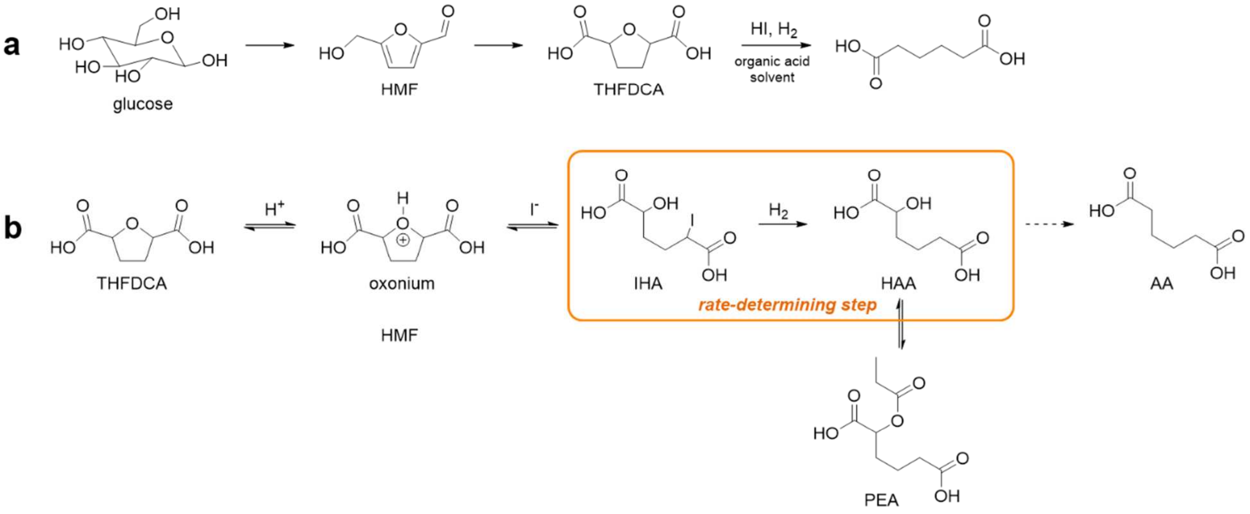
Abstract

We recently reported biomass-derived tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) as a potential renewable feedstock for adipic acid (AA) production by combining HI and molecular H_2 in organic acid solvents. However, the volatile and corrosive nature of HI, the catalyst, presents challenges in industrial implementation. In this work, we demonstrate an improved, less corrosive system with comparable AA yields (~ 87%) using Nafion and an iodide salt, e.g., LiI, NaI and KI. Kinetic and reactivity studies indicate that the activation of THFDCA's etheric C-O bond proceeds either by direct protonation at the surface of the solid acid or by liquid-phase protons which are transported from the surface of the solid acid to the bulk solvent through an ion-exchange process. The combination of a solid acid and an iodide salt functions as a controlled release mechanism for protons without sacrificing the effectiveness of HI, while significantly reducing the corrosiveness of the reaction mixture. Further, the spent Nafion can easily be separated from the reaction mixture and regenerated by ion-exchange with minimal loss in reactivity.

1. Introduction

Adipic acid (AA), an essential monomer in the production of Nylon 66, is among the highest volume dicarboxylic acids in the chemical and polymer industries.[1, 2] In oxidation reactions to produce AA from crude oil, corrosive chemicals, e.g., nitric acid, and harsh conditions are required, which produce a stoichiometric amount of NO_x byproducts,[1-3] which are undesired due to being toxic air pollutants and potent greenhouse gases. With heightening regulations on harmful gas emissions, alternative and especially renewable routes for AA production are desired. Motivated by previous work on the HI/Pd catalysts,[4] we have recently developed a metal-free system to convert biomass-derived tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) to AA with 89% yield.[5] We demonstrated the cooperation between molecular H_2 and HI in organic acid media to selectively cleave C-O bonds of the ring without overhydrogenating the carboxylic acid side groups. Based on experimental and theoretical findings, we proposed that the ring-opening reaction proceeds via equilibrated protonation and iodide addition followed by an irreversible metal-free H_2 activation step with only 2-(1-oxopropoxy)hexanedioic acid (PEA), or the ester between the organic acid solvent and 2-hydroxyadipic acid (HAA), as the only observed intermediate. [5]

We attributed the high AA selectivity to: (1) the strong acidity of HI and the strong nucleophilicity of I^- to protonate THFDCA and cleave C-O single bonds by an S_N2 halogenation in an organic acid solvent, respectively, and (2) the selective activation of molecular H_2 to remove C-I bonds without hydrogenating the carboxylic acid groups.[5] Although this process is efficient and selective, the corrosive and volatile nature of HI poses a significant barrier for industrial implementation. Thus, replacing HI with materials that are less corrosive and easier to separate from the reaction mixture, while maintaining high selectivity, could render this synthetic route more viable. One possibility is the employment of solid acids and iodide sources. This reduces the need for co-feeding large quantities of a corrosive acid (HI) while maintaining the essential components of the reaction system. Alternatively, supported bifunctional catalysts which contain both metal and acid sites, e.g., Pd/ZrP,[6] Rh-ReO$_x$,[7-9] Ir-MoO$_x$,[10] Ir-ReO$_x$,[11] and Pt-MoO$_x$,[12] are a promising class of catalysts for ring-opening, which have been studied extensively for the selective ring-opening of hydroxymethyl (tetrahydro)furans, e.g., tetrahydrofurfuryl alcohol (THFA), to aliphatic α,ω-diols. Based on the structural similarity between these hydroxylated substrates and THFDCA, these catalysts have the potential in catalyzing selective ring-opening toward AA, where acid sites generated by metal oxides (ReO$_x$ or MoO$_x$) activate etheric C-O bonds of the ring and metals perform the required hydrogenation reactions.[8] To this end, Tomishige et al. found that TiO$_2$-supported Pt-MoO$_x$ catalyst can catalyze some AA formation from FDCA, rather than from THFDCA, although selectivities are significantly lower than those from hydroxymethyl tetrahydrofurans (21% versus 99%).[12]



Scheme 1. AA formation from biomass-derived feedstocks from (a) glucose (dashed box emphasizes the ring-opening and hydrodeoxygenation steps without hydrogenation the COOH groups), and (b) tetrahydrofuran-2,5-dicarboxylic acid (THFDCA), illustrating the proposed reaction mechanism with C-I bond scission being the rate-determining step.[5] HMF = 5-hydroxymethylfurfural, THFDCA = tetrahydrofuran-2,5-dicarboxylic acid, IHA = 2-iodo-5-

hydroxyhexanedioic acid, HAA = 2-hydroxyadipic acid, PEA = 2-(1-oxopropoxy)hexanedioic acid, AA = adipic acid.

In this work, we present an experimental study that demonstrates a combination of an iodide salt and a solid acid is able to replace HI and remains effective in catalyzing the ring opening of THFDCA to AA. Although very active for THFDCA conversion, we show that supported metal/metal oxide composite catalysts tend to overhydrogenate THFDCA, removing one of the carboxylic acid groups prior to ring opening. Nafion is shown to be an effective proton source for ring-opening of THFDCA in the presence of an iodide salt. The ring opening reaction likely occurs following a similar mechanism as in the HI case either at the surface of Nafion or in the bulk solvent by protons transported from Nafion via ion exchange with the iodide salt.

2. Methods and Materials

2.1 Reactivity evaluation

Reactions were conducted in 50 mL stainless steel high pressure vessels (Parr Instrument Company) with magnetic stirring. The temperature profile of the reactor is controlled by a PID controller. A typical catalytic test was conducted by preparing 1 wt% THFDCA (CarboSynth, 98%) in 15 mL propionic acid (Sigma-Aldrich). Hydriodic acid (Sigma-Aldrich, 57 wt% in water) or lithium iodide (Alfa Aesar, 99%) was added to the mixture to reach a final concentration of 0.3 M. An initial sample was taken and analyzed in HPLC. The mixture was then transferred to the reactor (50 mL) equipped with a Teflon insert, a Teflon-coated thermocouple, a Teflon-coated magnetic stir bar and a predetermined amount of Nafion. The reactor was sealed and purged three times with N_2 and three times with H_2. Finally, the reactor was pressurized to 500 psi, and placed in a ceramic band heater and on a magnetic stir plate. The reactor was then heated to the set point (~20 min heat ramp) and left to react for the desired reaction time (typically 4 h unless otherwise specified). After reaction, the reactor was quenched in an ice bath until temperatures reached ~25 °C. The solution was then filtered from the solid acid and analyzed with high performance liquid chromatography (HPLC). Nafion was removed, washed in solvent, dried, and stored for further analysis. The washed, dried, spent Nafion beads showed no visible change in shape or size, with minimal coloration.

2.2 Analytical Procedures

An HPLC (Alliance Waters System e2695) equipped with a Bio-Rad Aminex HPX-87H (300 mm × 7.8 mm) column and a refractive index detector was used for analyzing the concentrations of reaction species. 5 mM H_2SO_4 was employed as the mobile phase, while maintaining the column at 50 °C. Samples were prepared by diluting post-reaction mixtures 1:10 in sub-micron filtered HPLC-grade water prior to injection. Calibration curves for the various species were made by creating solutions of known concentrations.

For identification of unknown products, an HPLC equipped with a mass spectrometer (HPLC-MS, Agilent 6120) and a Bio-Rad Aminex HPX-87H (300 mm × 7.8 mm) column was used. Solutions were prepared in the same way as described above, although 1% formic acid was chosen as the mobile phase due to compatibility with the mass spectrometer.

Carbon balance was computed based on the converted carbon, according to the following equation:

$$\text{carbon balance} = \frac{\sum_j N_j C_j}{N_{\mathrm{R}}(C_{i,\mathrm{R}} - C_{f,\mathrm{R}})} \cdot 100\% \qquad (1)$$

where the N_j is the carbon number in product j (in mol carbon/mol), C_j is the concentration of product j formed during reaction (in mol/L), C_{R} is the carbon number of the reactant (in mol carbon/mol), $C_{i,\mathrm{R}}$ is the initial concentration of the reactant (in mol/L), and $C_{f,\mathrm{R}}$ is the final concentration of the reactant (in mol/L). Yields and conversions were calculated according to the following equations.

$$Y_j = \frac{c_j}{c_{\mathrm{R},i}} \quad (2) \qquad X = \frac{c_{\mathrm{R},i} - c_{\mathrm{R},f}}{c_{\mathrm{R},i}} \quad (3)$$

2.3 Catalyst Preparation and Treatment

2.3.1 Preparation of supported metal catalysts

Rh-ReO_x/SiO_2 and Pt-MoO_x/SiO_2 catalysts were prepared by incipient wetness impregnation. Rh-ReO_x/SiO_2 catalysts were made by sequential impregnation of aqueous solutions of Rh(III) nitrate hydrate ($Rh(NO_3)_3 \cdot xH_2O$, Sigma Aldrich) and ammonium perrhenate ($NH_4ReO_4 . \cdot xH_2O$, Alfa Aesar) onto SiO_2 supplied by Fuji Silysia Chemical Ltd. First, impregnation of SiO_2 was conducted with an aqueous of $Rh(NO_3)_3$, and subsequently dried at 110 °C for 3 h. Then, Rh/SiO_2 was impregnated with aqueous NH_4ReO_4, and the catalyst was dried again at 110 °C for 3 h followed by calcination at 500 °C for 3 h. The resulting catalyst has a 4 wt% total metal loading with a Rh/Re molar ratio of 2 based on the amount of Rh and Re source. Pt-MoO_x/SiO_2 catalysts were also prepared via sequential incipient wetness impregnations, where aqueous solutions of H_2PtCl_6 (Sigma-Aldrich) and $(NH_4)_6Mo_7O_{24} \cdot xH_2O$ (Alfa Aesar) were used. Similarly, after the initial impregnation of Pt on SiO_2, the catalyst was dried at 110 °C. After Pt/SiO_2 was impregnated with aqueous $(NH_4)_6Mo_7O_{24} \cdot xH_2O$, it was dried at 110 °C for 3 h, and calcined at 500 °C for 3 h, where the resulting metal loading was 4 wt% with a Pt/Mo molar ratio of 2 based on the amount of Pt and Mo source added.

2.3.2 Ion exchange procedures

Ion exchange of fresh, spent, or exchanged Nafion beads was conducted in an aqueous solution at room temperature. Spent Nafion catalysts were regenerated by ion-exchanging in 5 M H_2SO_4 (Sigma-Aldrich, 99.99%) where H_2SO_4 was in excess compared to the number of sulfonic acid sites in Nafion (H_2SO_4: sulfonic group in Nafion = 10), which was calculated using Nafion's ion exchange capacity (IEC) of 0.8 mmol H^+ g^{-1}. Spent Nafion beads (1.8 g ~ 0.0015 mol acid sites) and about 25 mL of 0.6 M H_2SO_4 (~0.015 mol H_2SO_4) were added to a 50-mL beaker. This mixture was allowed to stir for 3 h. The liquid was then removed by filtration, and the beads were washed thoroughly in double deionized (DDI) water. This exchange process was repeated for a total of three times. The Nafion beads were subsequently washed with DDI water for 3 times. After the third wash, the beads were dried at 110 °C for 3 h before being transferred and stored in a vial. Ion exchanges of fresh Nafion beads (proton form) to sodium form, denoted as [Na]Nafion, were carried out similarly, except for using an aqueous 5 M $NaNO_3$ solution (Sigma-Aldrich) with a Na^+/H^+ ratio of 10.

To test the effect of solvent on the ion exchange process and subsequently quantify the degree of dissociation of various homogeneous acids, the ion exchange process was also conducted in propionic acid. After [Na]Nafion was made, [Na]Nafion (1.8 g ~ 0.0015 mol Na^+) was added to 25 mL mixtures containing 0.015 mol HI, $HClO_4$ (Sigma-Aldrich, 70% $HClO_4$ in H_2O), or H_2SO_4 in propionic acid. After 3 h of stirring, the propionic acid was removed by filtration, and the beads were washed three times in propionic acid, followed by drying at 110 °C for 3 h. The beads were then stored in a vial for subsequent characterization or reaction. These HI, $HClO_4$ and H_2SO_4 exchanged [Na]Nafion catalysts are denoted HI-ex [Na]Nafion, $HClO_4$-ex [Na]Nafion, or H_2SO_4-ex [Na]Nafion, respectively.

Inductively coupled plasma mass spectrometry (ICP-MS) was used to identify the presence of metal ions in solution after reaction at high temperatures. Solutions were prepared by reacting 0.3 M of additive (HI, Nafion and lithium iodide, or lithium iodide only) in 15 mL propionic acid under 500 psi H_2 for 4 h in the absence of THFDCA. After reaction, the reactor was cooled to room temperature and transferred to a 50-mL beaker. Due to the incompatibility of the organic molecules and the instrument, the organic acid was removed by stirring the solution at 100 °C until all liquid was evaporated. DDI water was used to re-dissolve the remaining salts and was left to stir for 30 min before re-heating the mixture to 90 °C to remove the solvent, and this procedure was repeated for a total of three times. The remaining solid was dissolved in 15 mL of 2% aqueous HCl solution and transferred to a beaker, which was further diluted 1:100 with a 2% aqueous HCl solution before the ICP-MS analysis. Calibrations of Cr, Mn, Fe, Co, Ni, and Cu were prepared by diluting solutions of these metal salts of known concentrations. Wavelength dispersive X-ray fluorescence (XRF) was conducted on a Rigaku Supermini200 instrument in a He atmosphere.

3. Results & Discussion

3.1 Catalyst evaluation for THFDCA ring opening to AA

Our previous report demonstrated the cooperativity of molecular H_2 (500 psi) and HI (0.3 M) in organic acid solvents, catalyzing AA formation from THFDCA with yield of up to 89% at 160 °C (Table 1, Entry 1) due to the presence of strongly acidic protons and an iodide source. Replacement of HI with Nafion (0.3 M H^+, all cation concentrations with Nafion in this study were estimated based on the ion-exchange capacity, or IEC, of the polymer) and lithium iodide (0.3 M I^-) results in a similarly high conversion and AA yield (99% conversion and 87% AA yield) under identical conditions (Table 1, Entry 3). Moreover, similar AA production rates on both the Nafion/lithium iodide and HI systems were measured in the kinetic regime (0.53 versus 0.31 mol L^{-1} h^{-1} $site^{-1}$, Table 2, THFDCA conversion <15%). These data suggest that the reaction mechanism likely remains similar when replacing HI with a combination of Nafion and an iodide salt. In contrast to Nafion, homogeneous acids, e.g., H_2SO_4 and $HClO_4$, are ineffective when combined with lithium iodide (Table 2).[5] The sulfonic acid groups within Nafion's polymer membrane are chemically similar to H_2SO_4, suggesting that acid strength alone cannot account for Nafion's superior performance. Other sulfonic acid-based polymeric materials, e.g., Amberlyst, were not employed due to their low thermal stability.[13] In reactions with Nafion/lithium iodide, a carbon balance of 87% was achieved. Of the remaining carbon (13%), ~2% can be attributed to the formation of unconverted 2-(1-oxopropoxy)hexanedioic acid (PEA), an intermediate formed during reaction. The rest of the carbon (11%) remained undetected by HPLC analysis, which suggests oligomeric species might be formed during the reaction.

Consistent with our previous work, both an iodide source and a proton source are necessary for the AA formation from THFDCA with Nafion. When LiI is used alone, no reaction is observed (Table 1, Entry 2). Similarly, Nafion alone is (0.1 M effective H^+) unable to mediate the formation of AA from THFDCA at 160 °C (Table 1, Entry 4), suggesting the iodide component is indispensable. Changing the balancing cation of the iodide source from Li to Na or K results in minor differences in THFDCA conversion and AA yield (Figure 1), where conversion and yield from different iodide sources rank in the order of NaI > LiI > KI. Due to the large ion-channels of within the Nafion membrane (~1

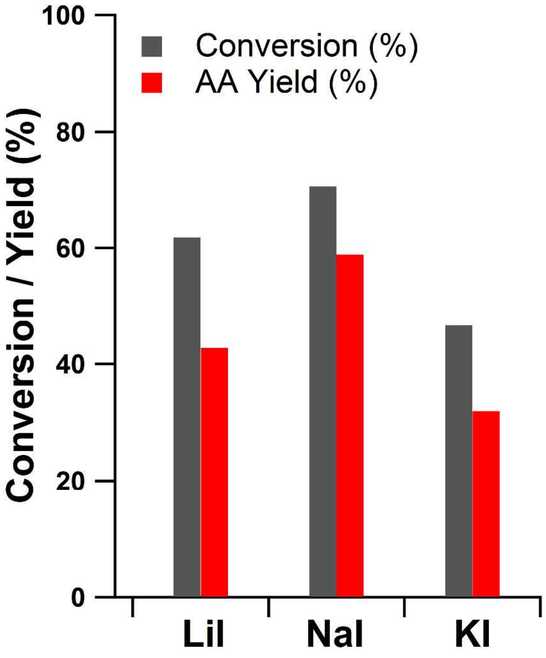


Figure 1. Effect of iodide sources on THFDCA conversion and AA yield. Conditions: 1 wt% THFDCA in 15 mL propionic acid using 0.1 M of each iodide salt, 1.8 g Nafion (0.1 M effective [H^+] based on IEC), and 500 psi H_2 at 160 °C for 3 h.

Table 1. THFDCA conversion over various catalytic materials.

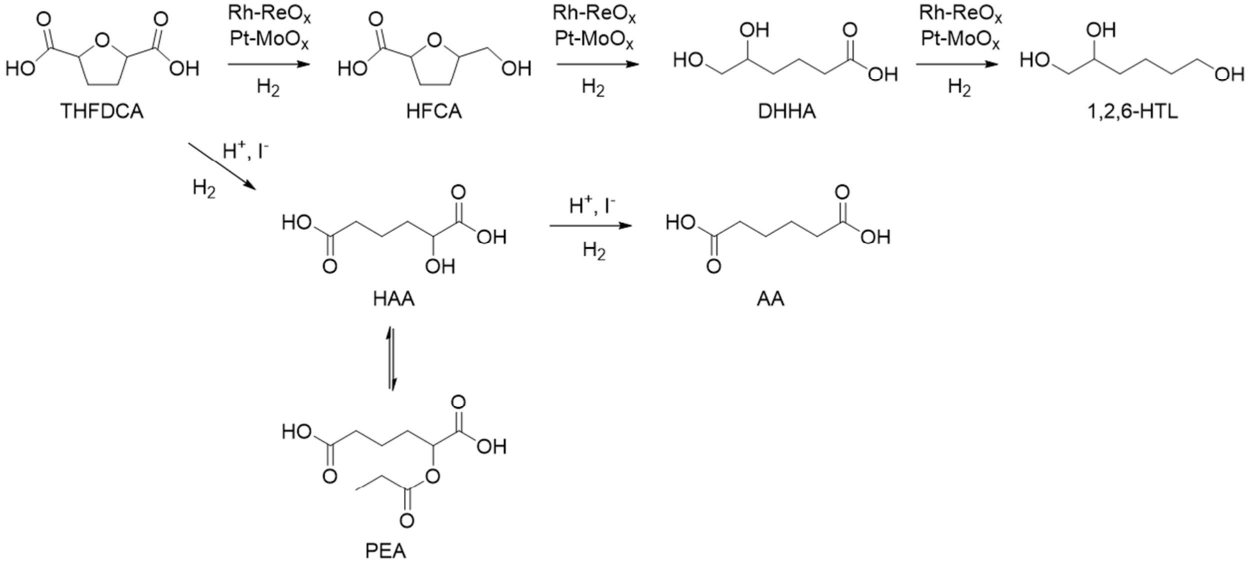
Entry	Catalyst	Solvent	Conversion (%)	AA Yield (%)	OH Products[e]	Carbon Balance (%)
1	HI[a,5]	Propionic acid	99	89	0	89
2	Lithium iodide	Propionic acid	0	0	0	-
3	Nafion[b] + Lithium iodide[c]	Propionic acid	99	87	0	87
4	Nafion only[b]	Propionic acid	0	0	0	-
5	Rh-ReO$_x$ (1:0.5)/SiO$_2$[d]	Propionic acid	3.1	0	0	-
6	Rh-ReO$_x$ (1:0.5)/SiO$_2$[d]	water	99	0	80	80
7	Pt-MoO$_x$ (1:0.5)/SiO$_2$[d]	Propionic acid	2.3	0	0	-
8	Pt-MoO$_x$ (1:0.5)/SiO$_2$[d]	water	99	0	83	83

Conditions: 1 wt% THFDCA in 15 mL solvent at 160 °C under 500 psi H_2 for 2 h. [a]0.3 M HI, [b]Effective proton concentration of 0.3 M H^+ based on IEC of Nafion, [c]0.3 M lithium iodide, [d]50 mg catalyst at 130 °C under 1000 psi. [d]50 mg catalyst at 160 °C under 500 psi. [e]OH denotes hydrogenated products, such as 5-hydroxymethyltetrahydrofuran-2-carboxylic acid (HFCA), 5,6-dihydroxyhexanoic acid (DHHA), and 1,2,6-hexanetriol (HTL).

Although metal/metal oxide composite catalysts, e.g., supported Rh-ReO_x and Pt-MoO_x, have been shown to be effective for ring-opening of hydroxymethyl tetrahydrofurans, we show that these catalysts are ineffective in converting THFDCA to AA due to the catalysts' propensity to hydrogenate the carboxylic acid groups in THFDCA prior to etheric C-O scission (Scheme 2 and Table 1). A number of metal/metal oxide composite catalysts, e.g., Rh-ReO_x/SiO_2 and Pt-MoO_x/SiO_2, have been shown to be highly selective (>90%) for ring opening of tetrahydrofurans with hydroxymethyl groups, e.g., tetrahydrofurfuryl alcohol to 1,5-pentanediol, at moderate temperatures (100 to 140 °C).[7-9] Under conditions similar to those previously used for ring opening over this class of catalysts (130 °C, 1000 psi H_2, 4 h reaction time), Rh-ReO_x/SiO_2 (4 wt% loading, Rh:Re = 0.5) in aqueous medium resulted in >99% THFDCA conversion with no detectable AA or 2-hydroxyadipic acid (HAA) formation. Instead, 3% selectivity to 5-hydroxymethyltetrahydrofuran-2-carboxylic acid (HFCA), 53% selectivity to 5,6-dihydroxyhexanoic acid (DHHA), and 24% selectivity to 1,2,6-hexanetriol (HTL) were found, suggesting that hydrogenation of the carboxylic acid groups is a dominant pathway. The formation of DHHA or HTL could stem from the ring-opening of THFDCA and subsequent hydrogenation of HAA; however, the sequence of hydrogenation and hydrogenolysis reactions cannot be concluded at high conversions. To assess whether HAA acts as an intermediate in this reaction, we conducted reactions at low conversions (100 °C) under otherwise identical conditions. After reaction, we observed only the formation of HFCA (~5.2% yield) and DHHA (~2.3% yield) at 10% conversion, suggesting that hydrogenation precedes ring-opening. In contrast, THFDCA conversion proceeds through PEA as the only observed intermediate in the

Nafion/iodide system. For example, low-conversion measurements at 100 °C using Nafion (0.1 M H^+) and 0.3 M LiI in propionic acid resulted in only two detected products, i.e., AA (4.9%) and PEA (3.1%). Although HAA is not observed directly, PEA's formation suggests that HAA does indeed form but is quickly converted via esterification with propionic acid. This is most likely due to the high concentration of propionic acid solvent and is consistent with our previous work.[5] Recently, Toste and coworkers reported that a combination of a rhenate, Pd/C, H_2 gas and an alcohol solvent could selectively convert glucarates to adipates;[14] however, a quite different mechanism is likely involved.[15-16]

Metal/metal oxide catalysts are not effective in converting THFDCA to AA in organic acid solvents, which was identified as a key element in the HI system.[5] We have previously shown that organic acid solvents ring open THFDCA by facilitating the protonation of its ether bond. However, reaction of THFDCA on Rh-ReO_x/SiO_2 in propionic acid solvent at 160 °C under 500 psi H_2 (similar conditions to our previous work)[5] led to only 3% THFDCA conversion and no detectable amount of AA. The lack of reactivity in propionic acid could be due to the fact that ReO_x does not contain sufficiently strong Brønsted acid sites to protonate THFDCA. Recently, TiO_2-supported Pt-MoO_x catalysts were used by Tomishige et al. with modest success in producing AA from FDCA (rather than THFDCA).[12] Our results suggest that Pt-MoO_x/SiO_2 performs similarly to Rh-ReO_x/SiO_2 in converting THFDCA to AA in aqueous media, i.e., COOH hydrogenation precedes etheric C-O bond scission (Table 1). It should be noted, however, that the system employed in this work and that used by Tomishige et al. contain some key differences, such as the catalyst support (TiO_2 vs. SiO_2), the starting material (FDCA vs. THFDCA), and reaction temperature, all of which could lead to the difference in the observed product distribution. The high selectivity we observe toward COOH hydrogenation over these metal/metal oxide catalysts is consistent with previous studies, where Pd-ReO_x catalysts were shown to selectively reduce carboxylic acid groups to alcohol groups.[17] Thus, our results suggest that metal/metal oxide composite catalysts may not be viable candidates for selective ring-opening of ring saturated furanics with carboxylic acid side groups because they preferentially hydrogenate the COOH groups. In contrast, the combination of Nafion and an iodide salt is active and selective for the ring opening of THFDCA to AA.



Scheme 2. Pathways from THFDCA demonstrating the preferential COOH hydrogenation over Rh-ReO_x or Pt-MoO_x catalysts and etheric C-O scission when iodide, molecular H_2, and a proton source are used.

Table 2. AA Formation rates with various proton sources.

Entry	Acids	AA Rate (mol L^{-1} h^{-1} $site^{-1}$)
1	$HClO_4$	0
2	H_2SO_4	0

3	HI	0.31
4	Nafion[a]	0.53

Conditions: 1 wt% THFDCA, 0.1 M H^+, and 0.3 M iodide (by addition of lithium iodide) in propionic acid at 100 °C under 500 psi H_2. AA rates are normalized to proton concentration. Conversions of THFDCA in these rate measurements were maintained below 15%.

3.2 Mechanistic insights into Nafion catalyzed AA formation

The ability to independently vary the concentration of proton and iodide can provide further mechanistic insights into their respective roles in the ring opening of THFDCA. Our previous report proposed that the ring-opening of THFDCA proceeded by equilibrated steps involving protonation, iodide substitution, and C-I hydrogenolysis (Scheme 1b), where experimentally determined reaction orders for AA formation led to the following rate expression:[5]

$$r_{\mathrm{AA}} = k[\mathrm{THFDCA}][\mathrm{HI}]^2 P_{\mathrm{H_2}}$$

The second-order dependence on the concentration of HI is rationalized by HI's dual role in the reaction, acting as both a proton source and an iodide source, both of which were proposed to have a first-order rate dependence. Upon dissociation of HI in propionic acid into H^+ and I^-, H^+ protonates the ether bond in THFDCA to form an oxonium ion intermediate, and I^- subsequently cleaves the C-O bond via nucleophilic substitution forming a C-I bond as a result. The subsequent hydrogenolysis of the C-I bond likely represents the rate-determined step. When HI is added to the reaction, however, the reaction orders of proton and iodide cannot be independently determined because they originate from the same source and thus have equal concentrations. The current system, consisting of independent proton (Nafion) and iodide sources (iodide salts), can probe the validity of our proposed reaction mechanism because separate reaction orders of proton and iodide can be determined by independently varying the concentrations of each component. To probe the reaction order of proton, initial rates of AA at low THFDCA conversions (≤15%) versus proton concentration (0 to 0.3 M H^+) were determined while holding iodide concentration constant at 0.1 M. The reaction order of proton was determined to be 1.1 ± 0.1 (Figure 2a). Following a similar procedure, a reaction order of 1.1 ± 0.1 was measured for iodide by varying iodide concentration from 0 to 0.3 M (Figure 2b). It should be noted that the identical expressions for fitted lines in concentration dependence studies of H^+ and I^- in Figure 2 are coincidental. We furthermore verified the reaction order of molecular H_2 in the Nafion/iodide system (~1st order, Figure S1), suggesting the rate-determining step remains unchanged. Thus, with the independently determined reaction orders for proton and iodide, the overall rate expression can be revised to:

$$r_{\mathrm{AA}} = k[\mathrm{THFDCA}][\mathrm{H}^+][\mathrm{I}^-]P_{\mathrm{H}_2}$$

which is consistent with the second order dependence on the HI concentration in our previous work.[5]

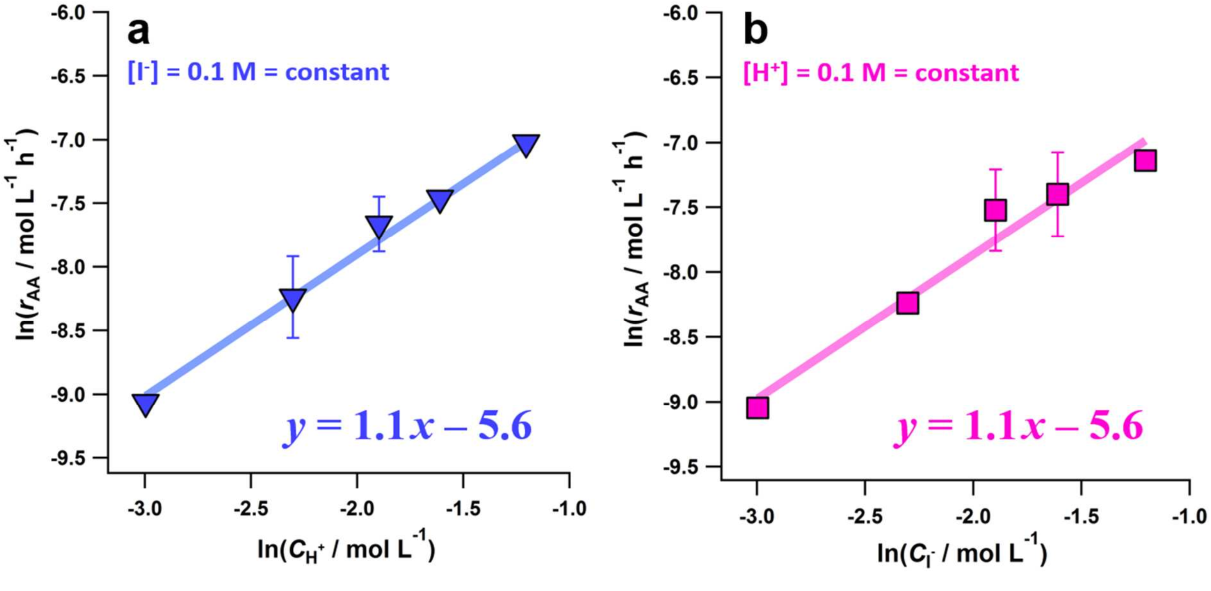
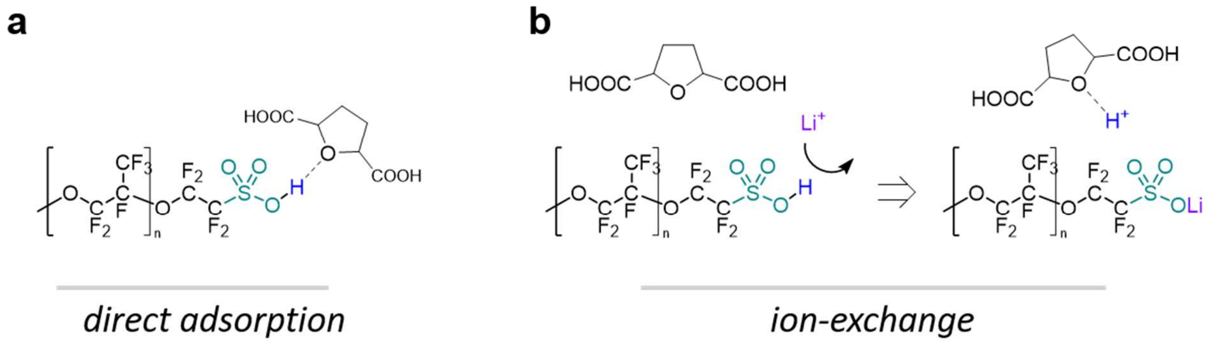


Figure 2. Reaction order with respect to (a) Nafion (proton concentrations based on IEC) at 0.1 M iodide concentration and (b) iodide at 0.1 M proton concentration (based on IEC of Nafion).

Conditions: 1 wt% THFDCA in 15 mL propionic acid at 100 °C under 500 psi H_2 for 4 h. All THFDCA conversions remained at or below 15%.

Conceptually, replacing HI with a solid acid only affects the delivery of protons to THFDCA. We have previously shown that only proton sources which can effectively dissociate in solution are able to facilitate the ring opening of THFDCA.[5] This was evident in cases where H_2SO_4 or $HClO_4$ was employed as the proton source in combination with lithium iodide, and minimal AA was observed. We attributed this to the poor dissociation of these mineral acids in organic acid media, which results in an insignificant number of free, available protons to activate the etheric C-O bond.[5] Solid acids, e.g., Nafion, introduce at least two possible pathways for the protonation of THFDCA (Scheme 3). One possibility involves heterogeneous chemistry (Scheme 3a) where THFDCA adsorbs and gets protonated onto the sulfonic acid groups tethered to the polymer backbone of Nafion. Alternatively, protons from Nafion could be transported to the bulk solvent via ion exchange with metal cations of the iodide salt, i.e., Li^+, K^+, or Na^+ (Scheme 3b) and carry out the protonation in solution (homogeneous chemistry). To probe the underlying mechanism, we turned to elemental analysis and reactivity studies of supernatant solutions obtained after reaction.



Scheme 3. Schematic distinguishing two possible mechanisms, including (a) direct adsorption of THFDCA to the active site on the solid acid material (heterogeneous chemistry), or (b) ion-exchange and solution-phase mediated protonation (homogeneous chemistry).

X-ray fluorescence (XRF) analysis of spent Nafion reveal that cations from iodide salts are incorporated into Nafion after the reaction, which provides evidence that ion-exchange is prevalent under reaction conditions. Spent Nafion beads were analyzed by XRF to quantify the amount of proton exchanged by metal cations during reaction. Because XRF is insensitive towards Li due to its low atomic mass, we performed the reaction with Nafion (0.1 M H^+) and 0.3 M sodium iodide. After reaction at 160 °C for 2 h, the spent Nafion beads were washed with propionic acid, dried, and subjected to XRF analysis to estimate Na:F ratios. Spent Nafion reveals significant Na incorporation (a Na:F ratio of 0.050; Table 3). No detectable level of sodium was observed in fresh Nafion, which indicates that all Na species in spent Nafion is due to the ion-exchange during reaction. The degree of ion-exchange can be computed by comparing spent Nafion to Nafion whose acid sites were completely exchanged to Na-form (denoted as [Na]Nafion). [Na]Nafion was prepared by repeatedly exchanging fresh Nafion in aqueous $NaNO_3$ with a Na^+/H^+ ratio of 10 (see experimental section for procedure), whose Na:F ratio was determined to be 0.067. By comparing the two Na:F ratios, it can be concluded that ~75% of the exchangeable protons in fresh Nafion are replaced by Na^+ after the ring opening reaction of THFDCA, which is consistent with an ion-exchange mechanism. In all XRF measurements, S:F ratios remain similar, indicating that the Nafion composition is comparable in all cases and the structure remains intact after the reaction. Although XRF indicates that a significant number of protons are displaced by Na cations during reaction, elemental analysis cannot exclude the possibility of that a significant fraction of reaction occurs at the surface of Nafion (Scheme 3a).

Table 3. XRF measurements of ion-exchanged Nafion.

Nafion	**S:F ratio**[a]	**Na:F ratio**[b]

Fresh	0.077	0
[Na]Nafion[c]	0.083	0.067
Spent[d]	0.075	0.050
[Na]Nafion-H_2SO_4(H_2O)	0.082	0.001
Spent Nafion-H_2SO_4(H_2O)	0.076	0.001
[Na]Nafion-HI(PA)[e]	0.065	0.022
[Na]Nafion-H_2SO_4(PA)[e]	0.095	0.057
[Na]Nafion-$HClO_4$(PA)[e]	0.095	0.035

[a]S:F indicates the homogeneity and structural consistency of the Nafion structure. [b]Na:F ratio indicates the degree of sodium incorporation into the Nafion membrane. [c][Na]Nafion = fresh nafion ion-exchanged in excess aqueous $NaNO_3$, [d]Spent = Nafion obtained after 1.8 g Nafion (0.1 M H^+ based on IEC) was used in reaction at 160 °C with 0.3 sodium iodide in propionic acid under 500 psi H_2 for 2 h. [e][Na]Nafion-HI(PA), [Na]Nafion-H_2SO_4(PA), and [Na]Nafion-$HClO_4$(PA) denote [Na]Nafion that was subsequently exchanged in propionic acid with HI, H_2SO_4, or $HClO_4$, respectively.

A corollary of the ion-exchange mechanism is that the supernatant solution of the reaction mixture should maintain at least a fraction of the ring opening activity due to the exchange of active protons from the solid acid into the bulk solvent. To test whether protons remain active in solution after the ion-exchange process, we performed experiments using supernatant solutions obtained by removing the Nafion beads from post-reaction solutions via filtration. After a typical reaction (1 wt% THFDCA (0.15 g), Nafion (0.1 M H^+), 0.3 M lithium iodide, 500 psi H_2 in propionic acid, 160 °C for 2 h), Nafion beads were removed via filtration at room temperature to generate a supernatant solution containing the propionic acid solvent, unreacted THFDCA, produced AA, and lithium iodide. After additional THFDCA was placed in the supernatant solution (0.15 g), the solution was introduced back into the reactor, re-pressurized with 500 psi H_2, and left to react again at 160 °C. After 2 h, only 10% of the freshly added THFDCA was converted (5% AA yield, Entry 1 in Table 4), suggesting that either the supernatant solution did not contain available protons for reaction, or the active iodide ions had decomposed during the initial reaction rendering the solution inactive, or both. We have shown previously that iodides are thermochemically unstable and decompose readily under reaction conditions to form an inactive triiodide species, e.g., I_3^-, over time.[5] To compensate for the decomposition of iodide, a similar experiment was performed where both THFDCA (0.015 g) and lithium iodide (the same amount as in the initial reaction) was added to the supernatant solution prior to the second reaction. In this case, the THFDCA conversion rose to 33% with a 25% AA yield (Table 4, Entry 2), suggesting that a large portion of the iodide introduced prior to the first reaction decomposed while a significant number of active protons remained in the supernatant solution. To test whether a significant amount of protons remained in Nafion after reaction due to incomplete ion-exchange during the first reaction, a control experiment was conducted in which Nafion was not removed from the supernatant solution and additional THFDCA and lithium iodide was placed in reactor. This resulted in an almost identical THFDCA conversion and AA yield as compared to the case in which Nafion was removed (Table 4, Entries 2 & 3). This suggests that the vast majority of the active protons in Nafion were exchanged into the bulk solvent during the first reaction. This is consistent with XRF measurements, where significant cation incorporation was observed in spent Nafion. Although supernatant solutions maintain a significant number of active protons, full activity cannot be recovered simply by recycling the supernatant solution (72% yield versus 25% AA yield) even though Na replaces the majority of Nafion's protons during the initial reaction based on XRF analysis (Table 3). This suggests that direct THFDCA adsorption to Nafion's sulfonic acid groups could be at play during the initial reaction.

Table 4. Supernatant solutions' activity in THFDCA conversion and AA yield.

Entry	**Conv. 1 (%)**	**Yield 1 (%)**	**Add I^-?**	**Remove Nafion?**	**Conv. 2 (%)**	**Yield 2 (%)**
1	75	62	No	Yes	10	5
2	86	72	Yes	Yes	33	25
3	88	73	Yes	No	35	27

Conditions: 0.15 g THFDCA and 1.8 g Nafion in 0.3 M lithium iodide in propionic acid at 160 °C under 500 psi H_2 for 2 h. Conv. 1 and Yield 1 denote the conversion and yield after the initial reaction containing both Nafion and lithium iodide, respectively. Conv. 2 and Yield 2 denotes the conversion and yield after second reaction by recycling the supernatant solution and adding additional THFDCA (0.15 g), respectively. Middle columns denote whether or not Nafion was removed and whether or not fresh lithium iodide was added to the supernatant solution prior to its use in the second reaction.

3.3 Regeneration and Benefits of Solid Acids

Although direct recycling the spent Nafion for THFDCA ring opening resulted in minimal activity due to the lack of protons on the spent Nafion beads (Figure 3), a regeneration step by reverse ion-exchange can completely restore Nafion's activity. Fresh Nafion (0.1 M H^+) in the presence of 0.3 M lithium iodide converted THFDCA (~89% conversion) to AA with ~78% yield at 160 °C after 4 h of reaction time. Recycling spent Nafion in the ring opening reaction resulted in a stark decrease in performance, converting only 20% THFDCA with 12% AA yield (Figure 3, pink bars), which is consistent with: (1) XRF results which show that ~75% of Nafion's protons are exchanged by metal cations, and (2) the insignificant change in activity in supernatant solutions with and without spent Nafion (Entries 2 & 3, Table 4). When comparing the activity of spent Nafion to that of [Na]Nafion (3.1% THFDCA conversion and 1.2% AA yield, Figure 3, yellow bars), it is clear that a small fraction of protons are still present on the spent Nafion, which is consistent with the XRF measurements (Table 3). Both spent

Nafion and [Na]Nafion can be regenerated by a reverse ion-exchange back to their proton forms in acidic aqueous environments (with H_2SO_4). Reverse ion-exchange was performed by mixing spent Nafion in excess aqueous H_2SO_4 ($H_2SO_4/Na^+ = 10$), followed by a washing step with DDI water (see experimental details). This method is effective in completely restoring [Na]Nafion's or spent Nafion's sulfonic acid groups to their proton form (denoted [Na]Nafion-$H_2SO_4(H_2O)$ and spent Nafion-$H_2SO_4(H_2O)$, respectively), as evidenced by XRF analysis which shows minimal Na incorporation (Table 3). The regenerated Nafion is able to achieve a THFDCA conversion of 91% and an AA yield of 79% (Figure 3, blue bars), confirming that the reactivity of Nafion is fully restored.

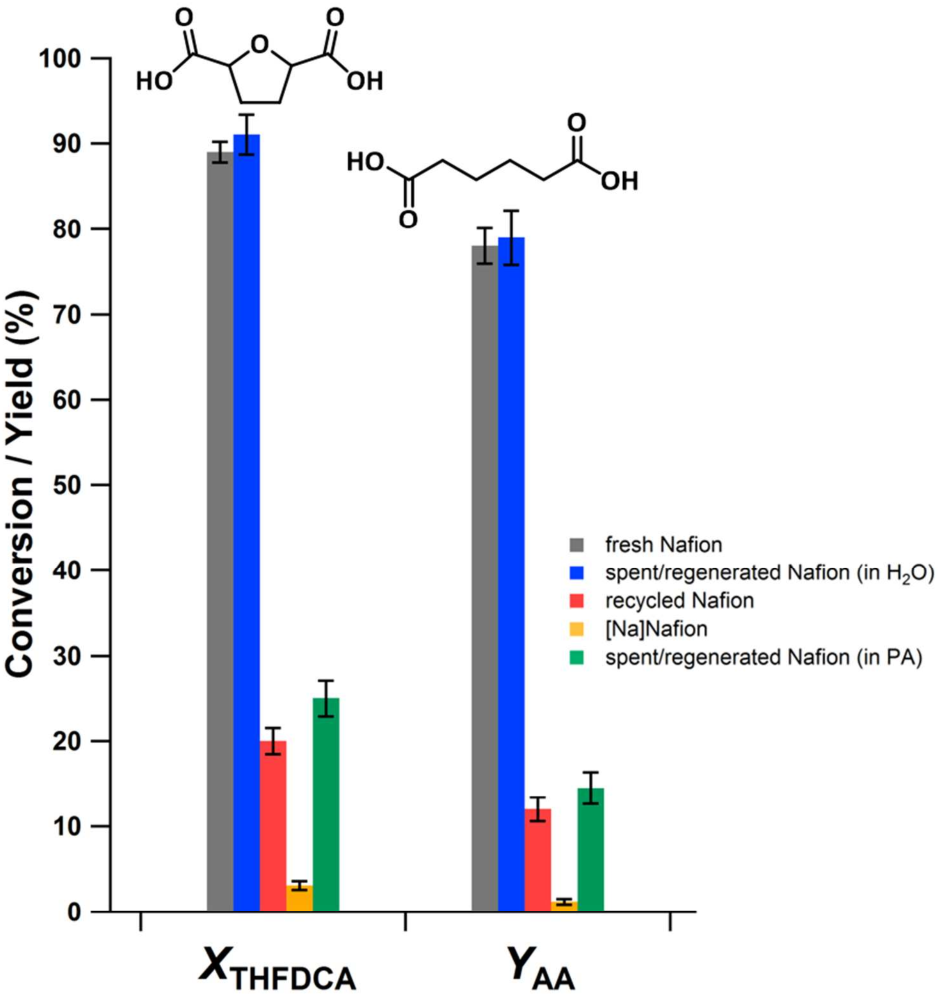


Figure 3. Comparison of fresh, spent, exchanged, and regenerated Nafion in THFDCA conversion and AA yield. Conditions: 1 wt% THFDCA in 15 mL propionic acid, 1.8 g Nafion (0.1 M H^+), 0.3 M lithium iodide at 160 °C under 500 psi H_2 for reaction time of 4 h.

Solvent has a decisive impact on the reverse ion-exchange process, which is attributed to the varying extent of dissociation of acids in non-aqueous media. Based on the pK_a of H_2SO_4 in water (~-3 for the first proton, ~2 for the second proton), nearly full dissociation into HSO_4^- and H^+ is expected. Thus, in an aqueous environment, ion-exchange occurs facilely with a substantial number of H_2SO_4's protons available to displace Na^+ cations in [Na]Nafion to restore its sulfonic groups to the proton form. When this same ion-exchange process is conducted in propionic acid, complete replacement of Na^+ in [Na]Nafion with H^+ cannot be achieved even with excess H_2SO_4 (H_2SO_4:Na = 10). Instead, XRF analysis demonstrates that H_2SO_4-exchanged [Na]Nafion in propionic acid (denoted [Na]Nafion-H_2SO_4(PA)) contains a significant amount of Na within the Nafion beads, where an Na:F ratio of 0.057 was measured, indicating that only 15% of Na was exchanged during reverse ion-exchange. This is consistent with the low activity of [Na]Nafion-H_2SO_4(PA) in THFDCA ring opening, with only a 25% THFDCA conversion and a 15% AA yield at 160 °C after 2 h of reaction (Figure 3, green bars). We hypothesize that the low level of ion-exchange in propionic acid is due to the low dissociation of H_2SO_4, as indicated by our recent computational results.[5]

This reverse ion-exchange process provides a general procedure to quantitatively compare the degree of dissociation of different mineral acids in organic solvents. For example, the degree of ion-exchange from [Na]Nafion to its proton form is dependent on the extent of dissociation of the mineral acid in a particular solvent. Acids that dissociate more completely are expected to produce a higher concentration of free, available protons to displace Na^+ in [Na]Nafion than acids that exist largely in their molecular form in the solution. We previously showed computationally that the dissociation constant of HI is significantly higher than that of $HClO_4$ or H_2SO_4 in organic acids.[5] To test this experimentally, reverse ion-exchange of [Na]Nafion (0.1 M Na^+) was conducted with each of the three acids of interest (HI, $HClO_4$, and H_2SO_4) in propionic acid (Figure 4). In this set of experiments, only one round of exchange was conducted using an acid/Na^+ molar ratio of 10. After washing the exchanged Nafion with propionic acid, XRF measurements indicated HI-exchanged [Na]Nafion in propionic acid (denoted [Na]Nafion-HI(PA)) contained the least amount of Na among the three samples (Na:F = 0.022, Table 3). [Na]Nafion-H_2SO_4(PA) and [Na]Nafion-$HClO_4$(PA) contained significantly more Na, with Na:F ratios of 0.057 and 0.035, respectively. These results suggest that HI dissociates to a much larger extent in propionic acid than both H_2SO_4 and $HClO_4$, which produces a higher concentration of available protons in the solution to displace Na^+. The elemental analysis by XRF is further supported by the catalytic performance of these acid exchanged [Na]Nafion samples. [Na]Nafion-HI(PA) resulted in the highest AA formation rate of 3.9×10^{-4} mol L^{-1} h^{-1}, which is more than a factor of the three higher than those with [Na]Nafion-H_2SO_4(PA) and [Na]Nafion-$HClO_4$(PA), at 1.3×10^{-5} mol L^{-1} h^{-1} and 9.2×10^{-5} mol L^{-1} h^{-1}, respectively (Figure 4, left axis). Thus, AA formation rate decreases in the order of [Na]Nafion-HI(PA) > [Na]Nafion-$HClO_4$(PA) > [Na]Nafion-H_2SO_4(PA), a relationship which parallels the decreasing percentage of protons that replace Na^+ during reverse ion-exchange process for each of the [Na]Nafion catalysts (Figure 4, right axis). It is interesting to note that although ~15% of Na^+ was replaced by H^+ after exchanging with H_2SO_4 in propionic acid, negligible AA production rate was observed. This indicates that not all protons in Nafion are equally active in mediating the ring opening of THFDCA.

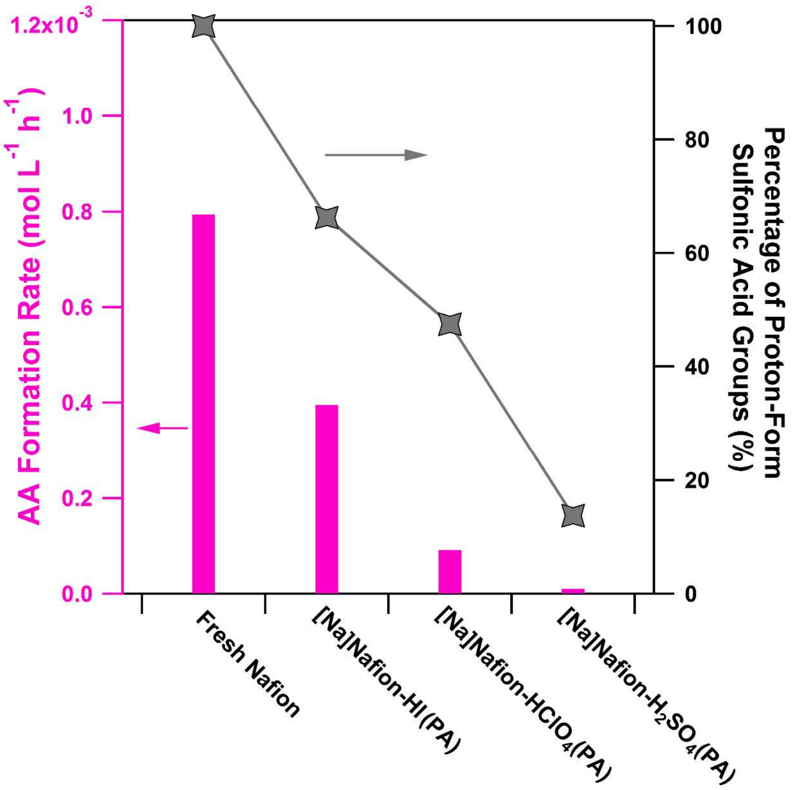


Figure 4. Effect of homogeneous acid on the ion-exchange of [Na]Nafion in propionic acid solvent, illustrating that HI more fully dissociates than $HClO_4$ or H_2SO_4, subsequently leading to higher AA formation rates. Conditions: 1 wt% THFDCA in 15 mL propionic acid, 1.8 g Nafion (0.1 M H^+ based on IEC), 0.3 M HI, 500 psi H_2 at 100 °C for 4 h. [Na]Nafion-HI(PA) = Nafion created by ion-exchanging [Na]Nafion in 1 M HI solutions in propionic acid, [Na]Nafion-$HClO_4$(PA) = Nafion created by ion-exchanging [Na]Nafion in 1 M $HClO_4$ solutions in propionic acid, [Na]Nafion-H_2SO_4(PA) = Nafion created by ion-exchanging [Na]Nafion in 1 M H_2SO_4 solutions in propionic acid. The right axis denotes the percentage of Na^+ cations which are replaced by protons during the reverse ion-exchange process in propionic acid.

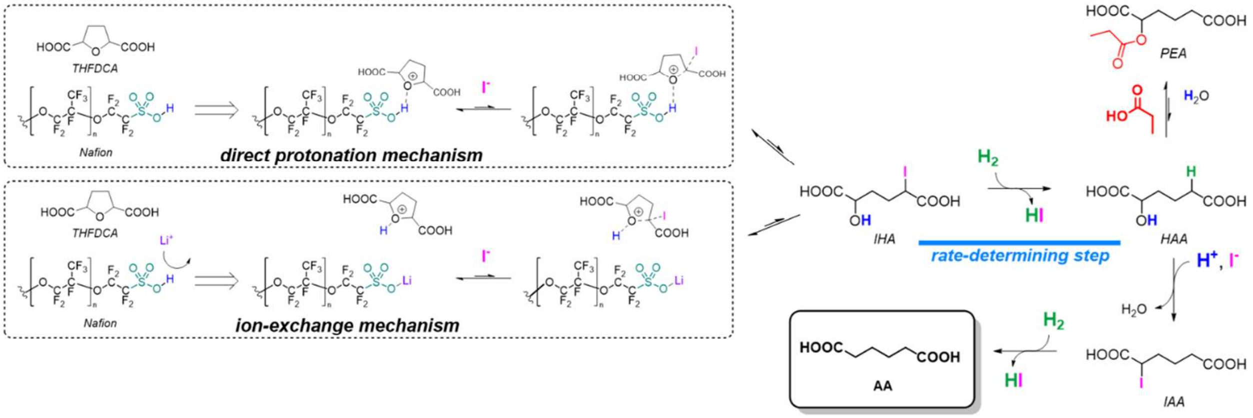
An added benefit of using solid acids in combination with iodide salts is that the corrosion of the reaction vessel is significantly reduced. After reaction at 160 °C with 0.3 M HI, ICP-MS analysis reveals that Fe, Cr, Ni, Mn, Cu, and Co accumulate in the solution at levels of ~558 ppm in total (Table 5). Fe ion has the highest concentration (255 ppm) among all metal cations (except for Li) in the solution after reaction. The accumulation of these ions can be attributed mostly to the presence of HI, rather than the organic acid solvent, because only 10.5 ppm Fe was detected in solution when only 0.3 M lithium iodide in propionic acid was employed. Replacing HI with Nafion with equivalent amount of H^+ (0.3 M H^+) and 0.3 M lithium iodide reduces the leaching of Fe into the reaction mixture by 35% (165 ppm vs. 255 ppm). Concentrations of other metals in the post-reaction solution such as Mn, Ni, and Cu levels were also reduced by similar fractions when compared with HI, although only a small drop in Cr concentration was observed. These results demonstrate that substituting solid acids and an iodide salt significantly reduces the levels of corrosion towards stainless steel reactors during reaction. This is likely due to the controlled release of protons into solution over the course of the reaction by ion-exchange as compared to using high concentrations of HI.

Table 5. Elemental analysis of post-reaction solutions measured by ICP-MS.

Additive	**Cr** [ppm]	**Mn** [ppm]	**Fe** [ppm]	**Co** [ppm]	**Ni** [ppm]	**Cu** [ppm]
lithium iodide	4.4	0.5	10.5	0.1	6.6	0.3
HI	62.8	12.7	254.8	21.1	201.9	4.6
Nafion[a] + lithium iodide	59.1	6.9	165.4	1.3	76.4	2.1

Conditions: 0.3 M additive in 15 mL propionic acid at 160 °C for 2 h under 500 psi H_2. [a]5.4 g Nafion (0.3 M H^+ based on IEC). ICP-MS samples prepared by controlled evaporation of propionic acid solvent followed by dilution in 2% HCl (see experimental methods).

3.4 Overall proposed mechanism for AA formation using Nafion and iodide salts



Scheme 4. Overall proposed mechanism for AA formation from THFDCA using solid acids and iodide sources suggesting (a) a direct protonation or (b) an ion-exchange mechanism.

Based on our experimental findings contained herein as well as in our previous work,[5] we propose that AA formation from THFDCA occurs first through protonation by the solid acid (Scheme 4) followed by iodide addition and metal-free H_2 activation, the latter of which is proposed to be rate-determining (Figure S1). The key difference between the current study and our previous work is that a solid acid, rather than homogeneous HI, acts as the proton source and possesses a first-order relationship with the AA formation rate. Based on reactivity studies and rigorous characterization, we propose that an ion-exchange mechanism is at play (Scheme 4b). Thus, cations in solution from the dissolved iodide salt are capable of displacing protons from the solid acid into bulk solvent to subsequently activate THFDCA's etheric bonds. However, this does not preclude the possibility of a direct adsorption mechanism, where THFDCA's etheric C-O bond could be directly activated by sulfonic acid groups (Scheme 4a). Indirect evidence of direct protonation stems from the observation that supernatant solutions are significantly less active than fresh Nafion, even though the majority of Nafion's protons exchange with Na cations during reaction. Although the use of Nafion invokes a subtle change in the proton delivery mechanism, the ring-opening mechanism largely remains the same compared to that when HI is used, because iodide still exists homogeneously in the liquid phase. This allows for facile cleavage of THFDCA's etheric C-O bond by an iodide ion once the ether bond has been protonated by Nafion (either via direct protonation of ion-exchange), forming IHA (Scheme 4). Since the reaction order of molecular H_2 (~1, Figure S1) remains unchanged, the diffusion-based ion-exchange process does not likely impact the overall rate to any significant degree; instead, C-I bond hydrogenolysis of IHA likely remains rate-determining, forming HAA and, subsequently, AA by sequential iodide substitution and C-I hydrogenolysis.

The use of a solid acid and an iodide source instead of homogeneous HI not only reduces the overall corrosiveness of the reaction system for AA production, but it could also lead to simplified separation processes. We demonstrate that Nafion can be regenerated and recycled, which is expected to reduce the cost of this synthetic route to AA. Although the active iodide phase in the chemistry degrades to inactive triiodide species over the course of the reaction due to thermochemical instability, iodide salts are abundant and low-cost reagents that could be treated as consumables. Despite the use of mildly corrosive solvents such as acetic acid or propionic acid, separation of organic acid solvents from the AA product is quite facile due to the major differences in volatility between the two, where the AA could be isolated by simply vaporizing the solvent.

4. Conclusions

We demonstrate that Nafion is an effective proton source for driving the ring-opening of THFDCA when combined with an iodide source and molecular H_2 in organic acid solvents, where selectivities of >85% are achieved. Without either the solid acid or the iodide source, the chemistry does not proceed. This finding is consistent with the first-order relationships of proton and iodide on AA formation. Based on a variety of characterization and activity studies, we hypothesize that two mechanisms are likely at play when employing Nafion as a proton source: (1) ion-exchange (homogeneous acid catalysis) and (2) direct protonation (heterogeneous, surface-mediated catalysis) mechanisms. The former mechanism is consistent with the observation that supernatant solutions, obtained after filtration of spent Nafion from post-reaction solutions, contain active protons for THFDCA formation. However, these supernatant solutions alone cannot fully recover the activity of fresh Nafion, despite the fact that most of Nafion's protons are transported to the bulk solvent during reaction as indicated by XRF analysis. The disparity in activity suggests that heterogeneous catalysis, in addition to homogeneous catalysis, is likely occurring during reaction. A key improvement of this system compared to HI is that Nafion can be regenerated via ion exchange with aqueous H_2SO_4 at room temperature. The employment of a solid acid in the current catalytic system reduces corrosion of the stainless-steel reactor walls via controlled release of active protons into solution rather than by co-feeding of a corrosive and volatile acid.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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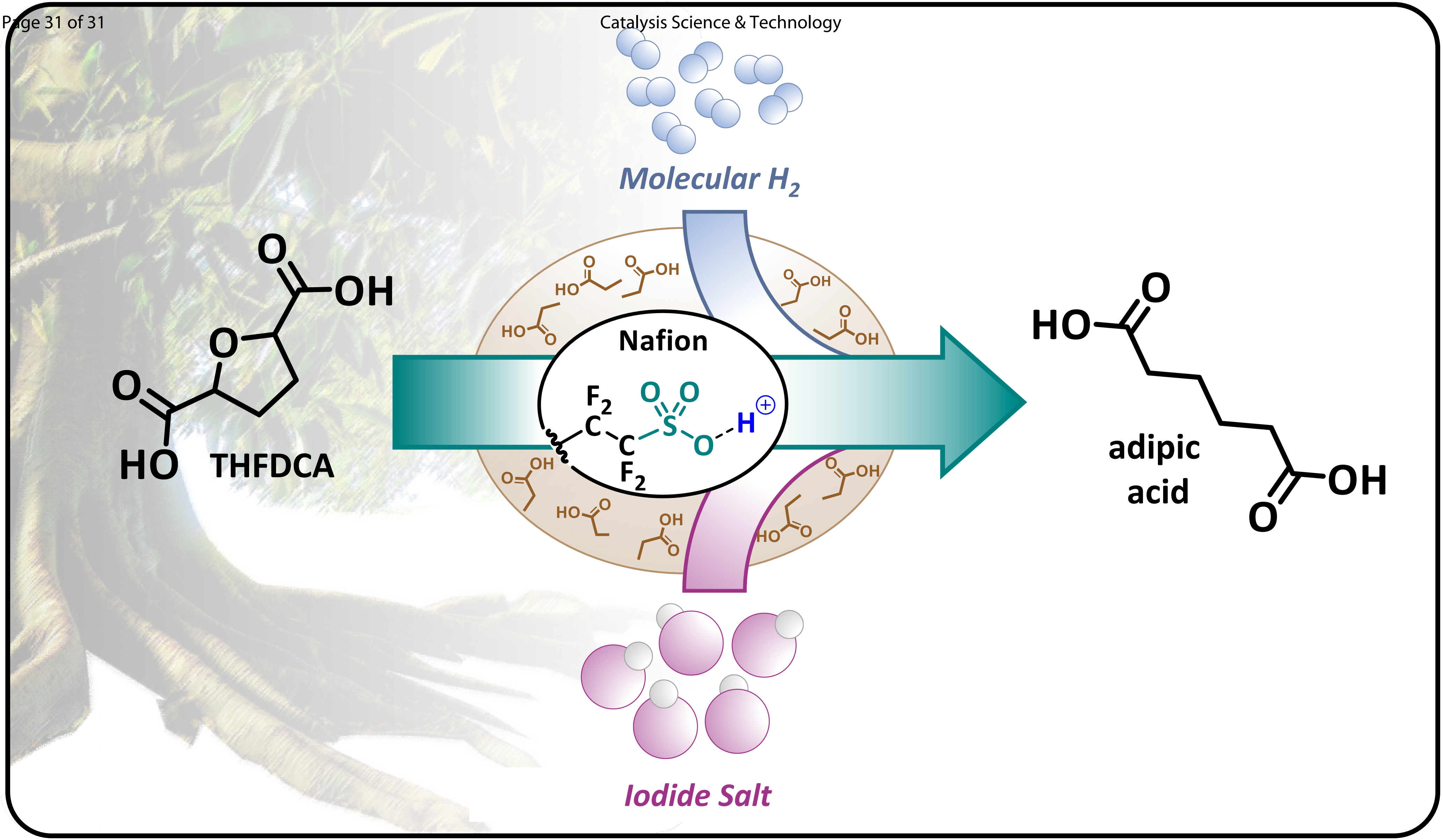
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