Hydrogen Storage Media with Value-Added Co-Products

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DE-EE-0011096

University of Southern California
Los Alamos National Laboratory
Brookhaven National Laboratory
California State University, Los Angeles

Project Goal

- **Project Goal: We will demonstrate a continuous operation reactor for the conversion of ethanol to potassium acetate and hydrogen** that will realize the first approach to liberate 2 equivalents of hydrogen from ethanol and establish it as a liquid hydrogen carrier that simultaneously produces a high-value co-product. This will enable ethanol as a value-positive one-way hydrogen carrier.

- **Ethanol Dehydrogenation**
  - While ethanol-to-ethyl acetate has been shown as a 2-way hydrogen carrier (PNNL), no 2-way carrier has been shown to be revenue-positive in the marketplace without subsidy. We will develop ethanol as a 1-way carrier, where its dehydrogenated co-product, eg. potassium acetate, has such high value as an agrochemical as to support revenue-positive hydrogen generation at scale, even if ethanol is a minor component of a C1 plant.

By co-producing a high value agrochemical, we will show a highly revenue-positive 1-way liquid hydrogen carrier.

- **Demonstration Reactor**
  - Commercializing ethanol-to-acetate will require a continuous reactor that can separate clean solid and gaseous products from a homogeneous liquid reaction.

With a working prototype, we can know mass and energy efficiency and longevity of the process.

- **Mechanistic Studies**
  - By understanding the molecular mechanism of our catalysis, we can suppress known side reactions.

We have shown that catalyst optimization can suppress side reactions, but we don’t know why.

Overview

- **Timeline**
  - Project start date: 1 March 2024
    (No funds received at time of writing)
  - Project end date: 28 February 2027

- **Budget**
  - Total project budget: $1,000,000
    - Total recipient share: $0
    - Total federal share: $1,000,000
    - FY24 DOE funds received: $0
    - FY25 DOE funds planned: $300,000
    - FY24 cost share funds received: $0
    - FY25 cost share funds planned: $0

- **Barriers**
- Master ethanol dehydrogenation
  - Realize high catalyst efficiency
    - Target: > 10^6 turnovers with efficient recovery
  - Extend ethanol technology to glycerol
- Demonstrate a continuous H_2 release process
  - Show in-line isolation of solid potassium acetate and hydrogen gas, each at usable purity
- Understand molecular mechanism
  - Leverage computational studies to understand and suppress Guerbet and Tishchenko side reactions

- **Partners**
  - University of Southern California (lead)
  - Brookhaven National Laboratory
  - Los Alamos National Laboratory
  - California State University, Los Angeles

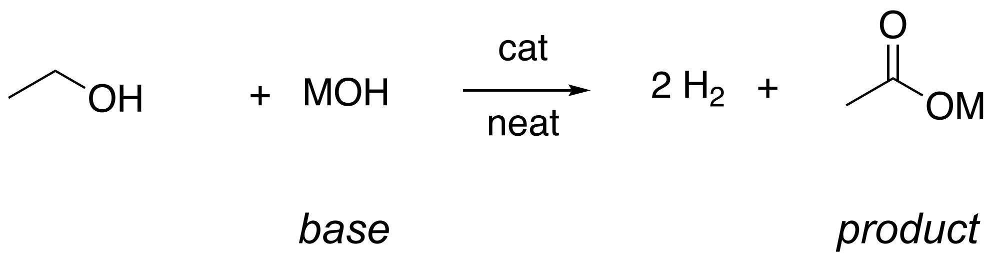
Potential Impact

- **Target Impact:** *Producing hydrogen on demand and driving down its cost are key hurdles in our national transition to clean energy infrastructure*.
  - Making hydrogen efficiently from liquid carriers is important to our ability to make H_2 fuel available in distributed locations, particularly for transportation applications.
  - Co-producing a high-value fine chemical along side H_2 subsidizes the total cost of plant operation, driving the aggregate cost of H_2 below \$1/kg, even potentially below \$0, even if the bulk of H_2 generated from the plant proceeds through a different carrier system, eg. formic acid-CO_2 as in our prior sponsorship (DE-EE0008825).

- **Objectives:**
  - (1) *Develop conditions for ethanol dehydrogenation*. We show here that ethanol is readily converted to acetate and 2 H_2 by reusable, homogeneous catalysts. We will develop this reaction to be a continuous operation process in which we can assess efficiency, product isolation, and pressurization.
  - (2) *Implement a continuous operation reactor for formation and separation of agrochemical co-products*. We will build a reactor that will enable the scalable, continuous operation of the reaction above and qualify its ability to produce high purity, pressurized H_2 and carboxylates.
  - (3) *Illustrate efficiency and product distribution for CO_2 re-reduction*. We will develop chemistry to flow CO_2 captured from our prior formic acid dehydrogenation back into our reactor and convert it to fuels using H_2 that could be generated on-site in off hours. Whereas agrochemical production won't fully meet H_2 demand in our envisioned use cases, our plant will also be dehydrogenating other carriers, eg. our C1 formic acid system.
  - (4) *Computational modeling*. We will use theory to resolve questions of chemical mechanism, such as pressurization effects and chemical selectivity in ethanol dehydrogenation, that might limit our ability to achieve high pressure and high selectivity in packages 1 and 2.

Potential Impact

- **Revenue Model:** Central to our hypothesis of value generation is the business case for our dehydrogenated co-products. This is our revenue model, based on 2023 bulk material prices in the United States.



Product	Alcohol Cost	Base Cost	Carboxylate Value	Retail H_2	Multiple	Market Size
Sodium Acetate	($43)	($125)	$90	$143	0.39	$181M
Potassium Acetate	($43)	($665)	$3,418	$143	4.0	$181M
Calcium Acetate	($43)	($409)	$10,140	$143	22	$62M

We envision deployment of our technology in a market such as Stockton or Long Beach, CA. Here we would be providing emerging, advantaged agrochemicals to impoverished, largely Latino farming communities of the California central valley.

Approach

- **Research Strategy**
  - Discover conditions for ethanol-to-acetate conversion (done!).
  - Determine product purity (versus Guerbet and Tishchenko pathways) for various catalysts.
  - Measure and optimize maximum catalyst turnover and response to pressurization. Optimize these for catalysts with high product purity.
  - Design and build a continuous operation reactor to produce H_2 and acetate salts from ethanol.
  - Verify our ability to cycle CO_2 and H_2 to formic acid over the same catalysts.
  - Use theory to understand and exploit how catalyst differences enable higher selectivity in ethanol dehydrogenation.

- **BP1 Goal** (2025): Demonstrate dehydrogenation of 200 mL ethanol to acetate (> 98% purity) with commensurate rate of H2 production. Report yield and purity of each product. Complete reactor schematic diagram and parts list.

- **BP2 Goal** (2026): Illustrate ethanol dehydrogenation in the demonstration reactor through 1M turnovers with > 99% acetate selectivity and H_2 of < 10 ppm combined impurities. Illustrate glycerol performance in analogous conditions.

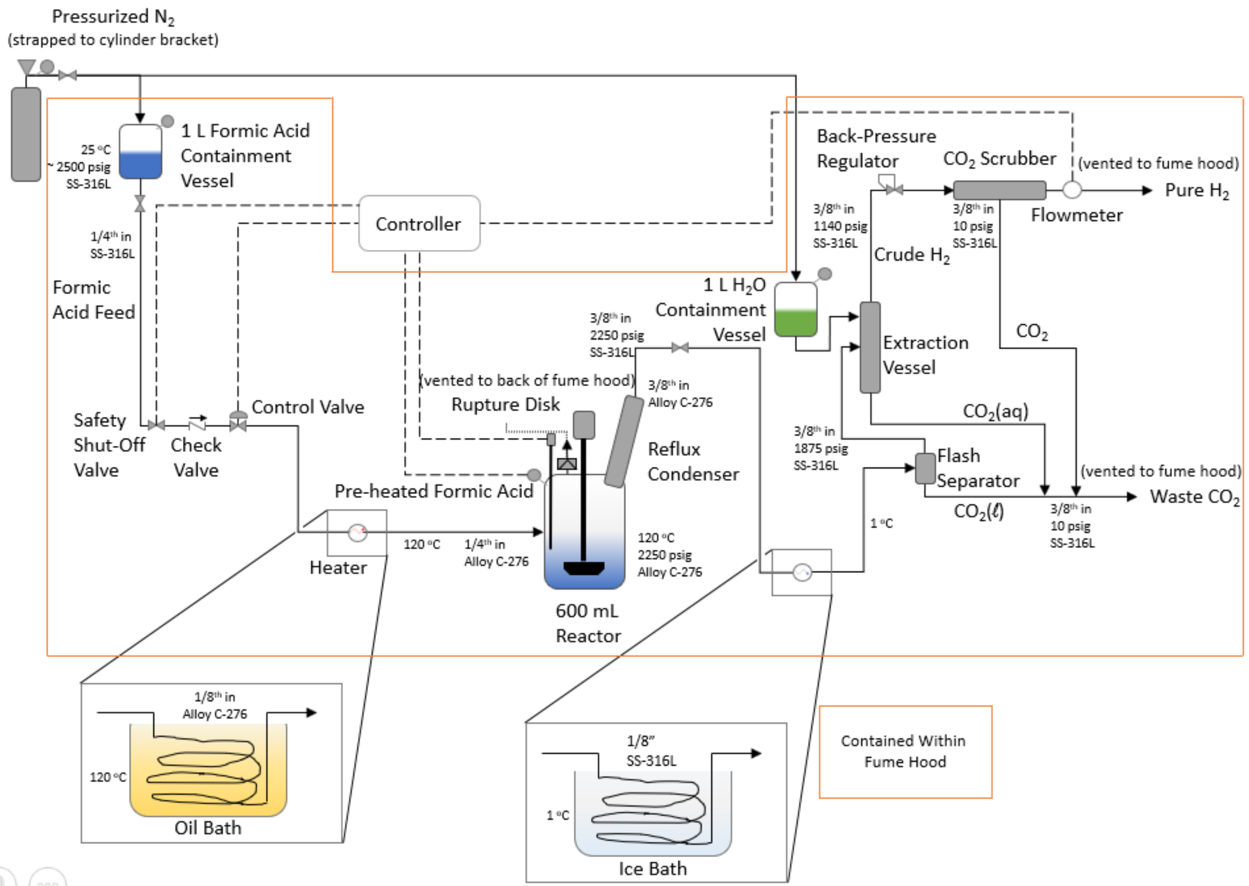
- **End of Project Goal** (2027): Quantify our H_2 output purity and compare against targets for regarding CO_2 and CO (< 5 ppm total) for alcohol dehydrogenation. Report carboxylate yield > 90%, 99% purity.

- **Core Project Team**: USC: Travis Williams, Rice Rander, Valeriy Cherepakhin; LANL: Robert Currier; Brookhaven: John Gordon, Zahid Ertem; CalState LA: Matthias Selke, Yangyang Liu.

Approach: Safety Planning and Culture

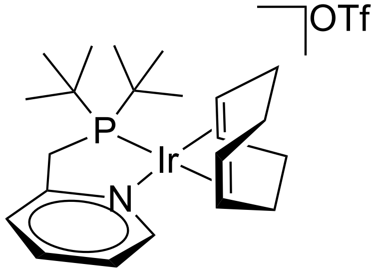
- HSP Review
  - Our formic acid dehydrogenation reactor was **reviewed and approved by the HSP in 2021**.
  - A modified design for this reactor will be submitted to HSP as soon as designs are completed.

- USC Office of Environmental Health and Safety
  - USC EHS inspects all laboratory facilities used for this project semiannually to ensure compliance of facilities with our HSP-approved standard operating procedure.
  - Williams (PI) ensures day-to-day compliance of personnel with our HSP-approved SOP.
  - Williams sits on the USC chemical safety committee, research safety oversight committee, and university compliance workgroup to ensure an excellent working relationship with EHS.
  - All safety incidents and near misses are reported to and investigated by EHS, then reviewed by the committees above, per EHS recommendations.
  - We have reported no H_2 safety incidents to EHS since the commencement of the prior project in 2019.



Schematic diagram of our HSP-approved continuous operation H_2 generation reactor, as designed for formic acid dehydrogenation

Accomplishment: Found Catalysts for Ethanol-to Acetate



1
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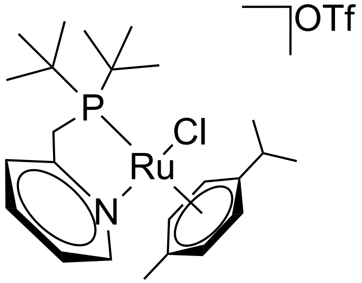

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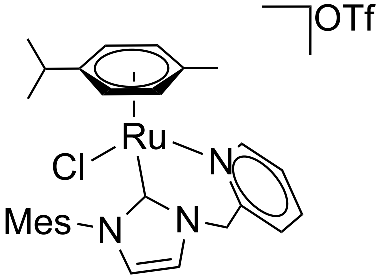

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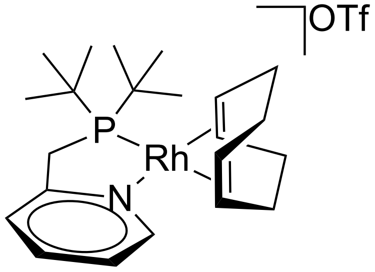

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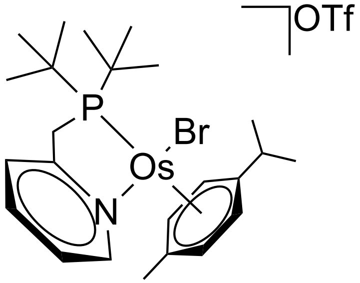

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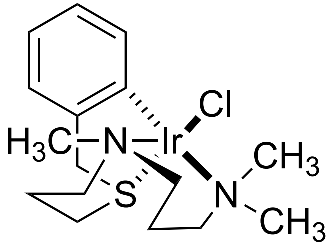

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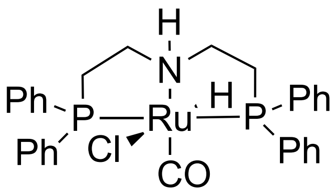

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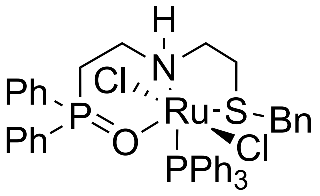

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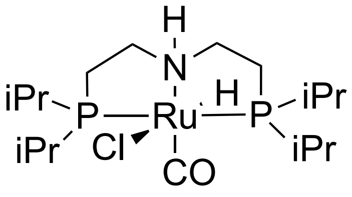

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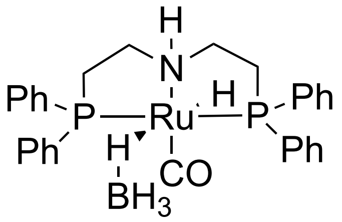


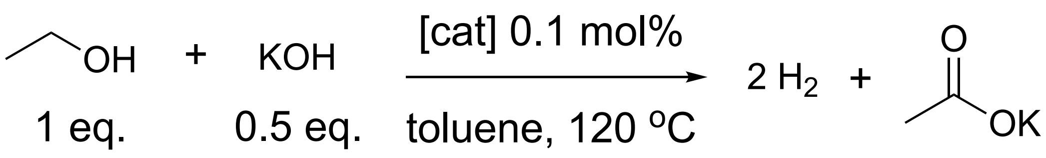
10
95%

- We have identified several catalyst systems that are efficient for the conversion of ethanol to acetate in a single pass at ambient pressure. The comprise both some of the proposed iridium systems and a family of both new and well-known ruthenium systems. The latter deliver superior performance at ambient pressure.

Moving from iridium to the less precious and less expensive ruthenium systems dramatically improves the sustainability profile of the overall process. Combining this with efficient catalyst reuse and recovery will make the process very appealing.

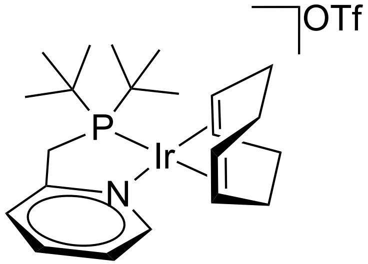
Accomplishment: Established Conditions for Self-Pressurization

- Gas compression costs can comprise ca. 50-80% of the retail cost of hydrogen, respectively for light or heavy vehicle filling (EERE). Exploiting the reaction entropy intrinsic to dehydrogenating a liquid carrier, we show that we can generate pressurized hydrogen from ethanol dehydrogenation.



Self pressurizing 0 - 30 bar

Entry	Cat[a]	EtOH (equiv.)	KOH (equiv.)	Yield % (AcO^-)[b]
1	**1**	1	0.5	50
2	**10**	1	0.5	98
3	**3**	1	0.5	
4	**3**	3[c]	0.5	
5	**10**	0.75	1	20
6	**10**	0.5	1	46
7	**10**	3[c]	0.5	99



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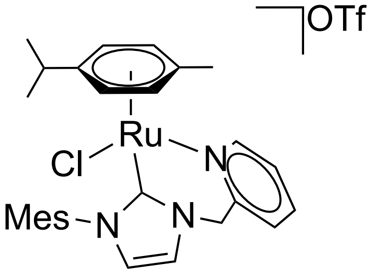

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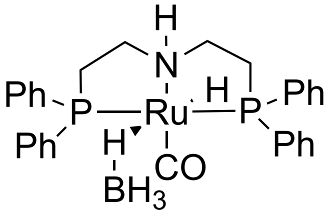

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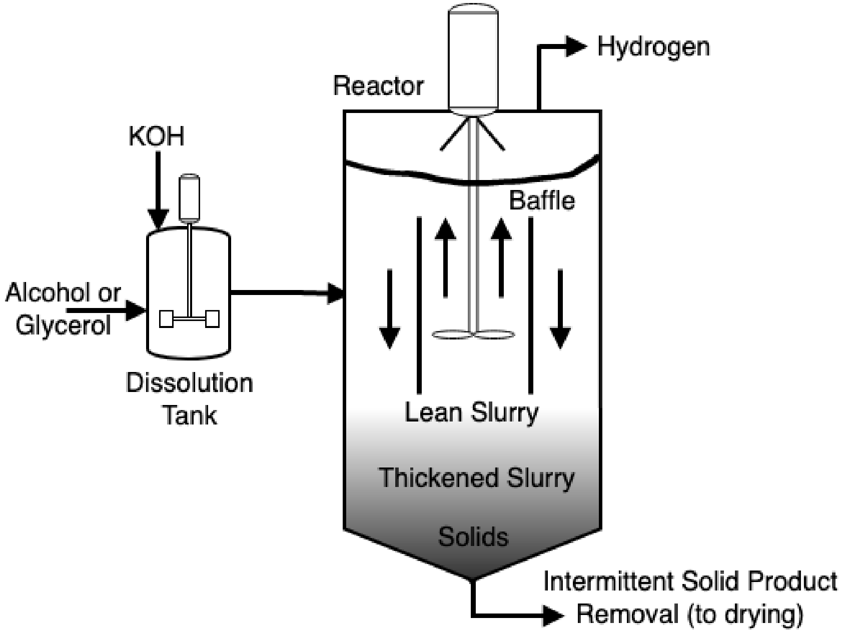
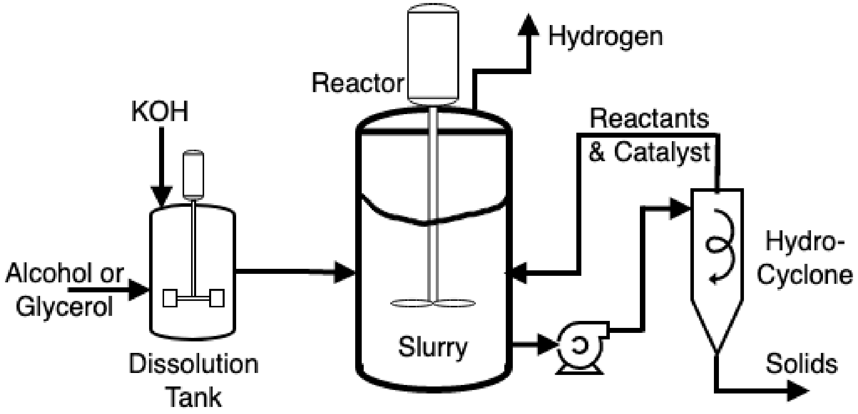
[a] *Catalyst loading based on moles of ethanol in entries 1 & 2; KOH 3 & 4*
[b] *Catalyst loading based on moles of KOH*
[c] *Neat ethanol*

Exploiting reaction entropy offsets compression costs for hydrogen delivery.

Progress: Conceptual Designs for the Continuous Reactor



Because of its sparing solubility in ethanol, a continuous gravimetric separation could separate a concentrated acetate solution from the bulk reaction, but residual catalyst and reagents would need to be re-collected and cycled in a downstream step.



Pumping a reaction/product suspension through a centrifugal separator would affect superior product separation but presents a more technically complex solution that could be more capital intensive.

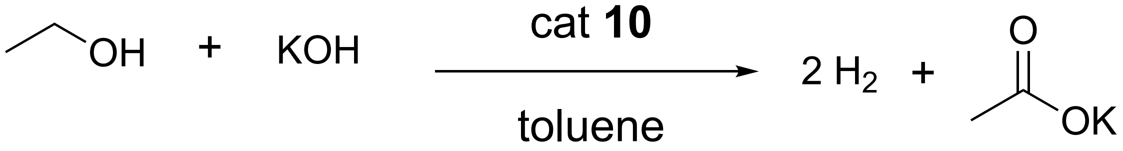
A Demonstration Reactor at USC from our formic acid project will be retrofitted for solids isolation. H_2 purification is already built in, as we have shown quantitative CO_2 / H_2 separation in DE-EE0008825.

Robert Currier, LANL

Progress: Determined Feasibility of Operating in an Excess Ethanol Situation

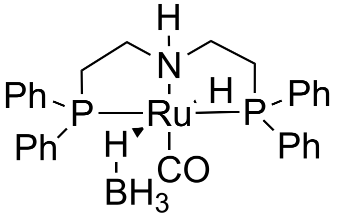
- Our envisioned process involves slow addition of hydroxide solution to a circulating ethanol solution with continuous acetate and H2 collection. This requires conditions that operate well in high ethanol and low hydroxide conditions.

Superior single-pass yields are observed in the requisite low [hydroxide] conditions.



Entry	EtOH (equiv.)	KOH (equiv.)	Temp (˚C)	Cat. Loading (mol%)[a]	Yield % (AcO^-)[b]
1	1	1	120	0.1	95
2	1	0.75	120	0.1	98
3	1	0.5	120	0.1	99
4	1	0.25	120	0.1	99
5	0.75	1	120	0.08	47
6	0.5	1	120	0.08	48
7	0.25	1	120	0.08	26
8[c]	1	0.5	80	0.1	14
9[c]	1	0.17	80	0.1	96

A high yield in neat ethanol is a key step toward a continuous operation process



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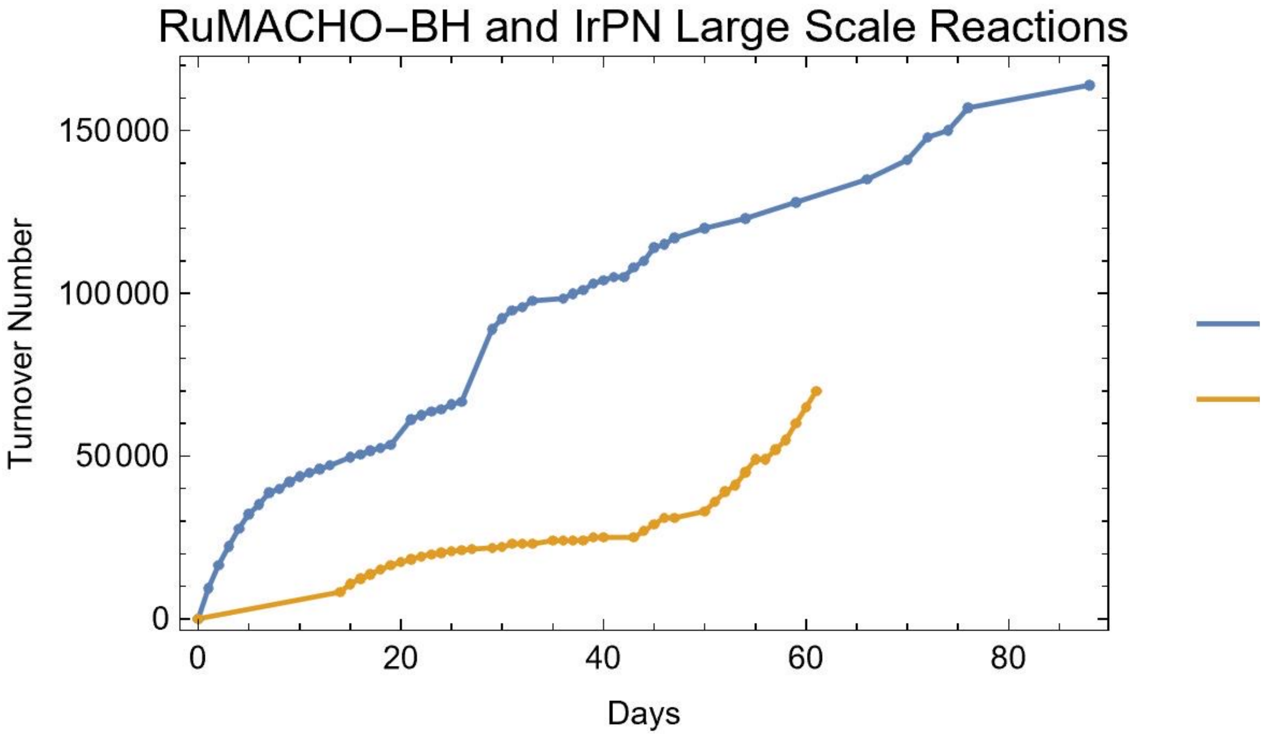
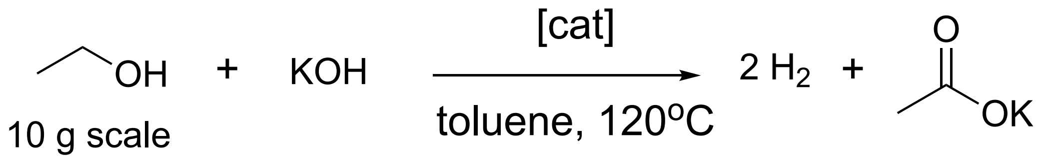
[a] *Catalyst loading based on moles of ethanol 1-4, KOH 5-7*
[b] *Based on moles of KOH (titration)*
[c] *Neat ethanol*

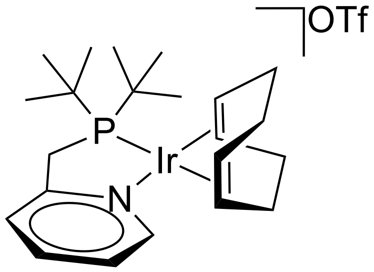
Progress: Measured a Baseline for Catalyst Longevity

- **Starting Point:** We have shown 55,000 and 168,000 turnover numbers (unoptimized) for respective lead ruthenium and iridium catalyst systems.





Entry	Cat.	Cat. Loading [a]	Total TON
1	**11**	5 ppm	168,000
2	**10**	0.1 mol%	55,000



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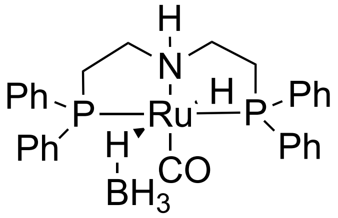

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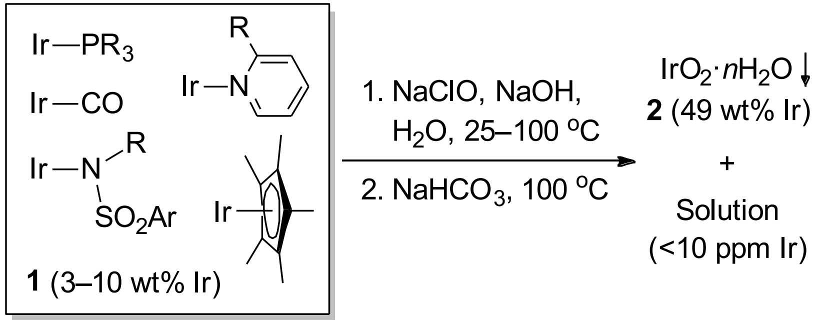
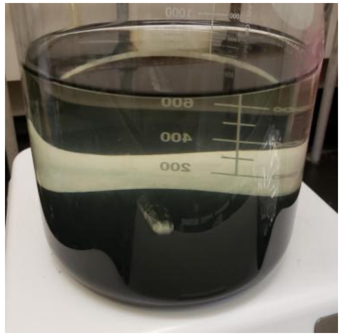
Accomplishment: A Viable Iridium Recycling Method

- We have reported the first scale-flexible process for recycling iridium-containing waste.
- Whilst we find no US vendor who will buy and recycle iridium waste (unlike Rh, Ru, Pd, Pt, and others), we see this as a key contribution to iridium sustainability.
- The procedure can be easily achieved with undergraduate-level training, beakers, stir bars, and high school-level apparatus.

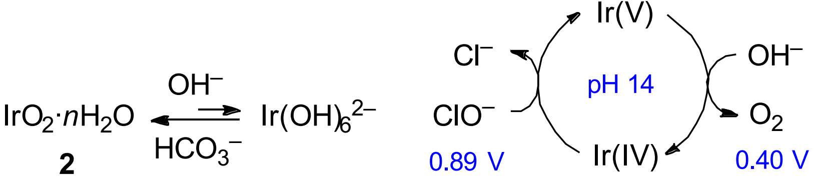


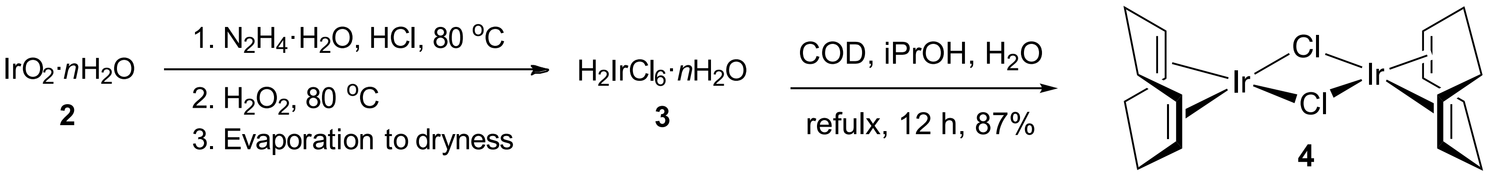
crude Ir waste



IrO_2-nH_2O

H_2IrCl_6-nH_2O





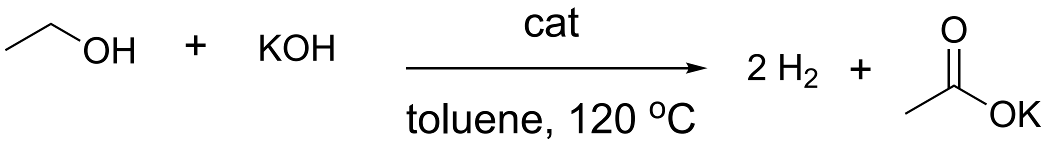
$[Ir(COD)IrCl]_2$

This appeared in *Green Chemistry* in 2024 as an RSC-designated “Hot Paper”.

Cherepakhin, Williams. *Green Chem.* **2024**, Advance Article, 10.1039/D4GC00151F.

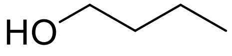
Progress: Mechanistic Work Will Address Observed Differences in Selectivity

- By documenting differences in reaction selectivity with different catalysts, we provide the foundational experimental observations necessary to start the proposed computational studies.
- We have observed that RuMACHO-BH (**10**) forms different species based on hydroxide loading. Each result in different reaction selectivity.

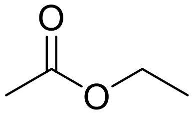


Entry	Cat.	EtOH (equiv.)	KOH (equiv.)	Yield % (AcO^-)	Other Products (%)
1	**1**	1	1	24	5%
2	**10**	1	1	95	<1%
3	**10**	1	0.5	99	<1%
4	**10**	0.5	1	48	4%

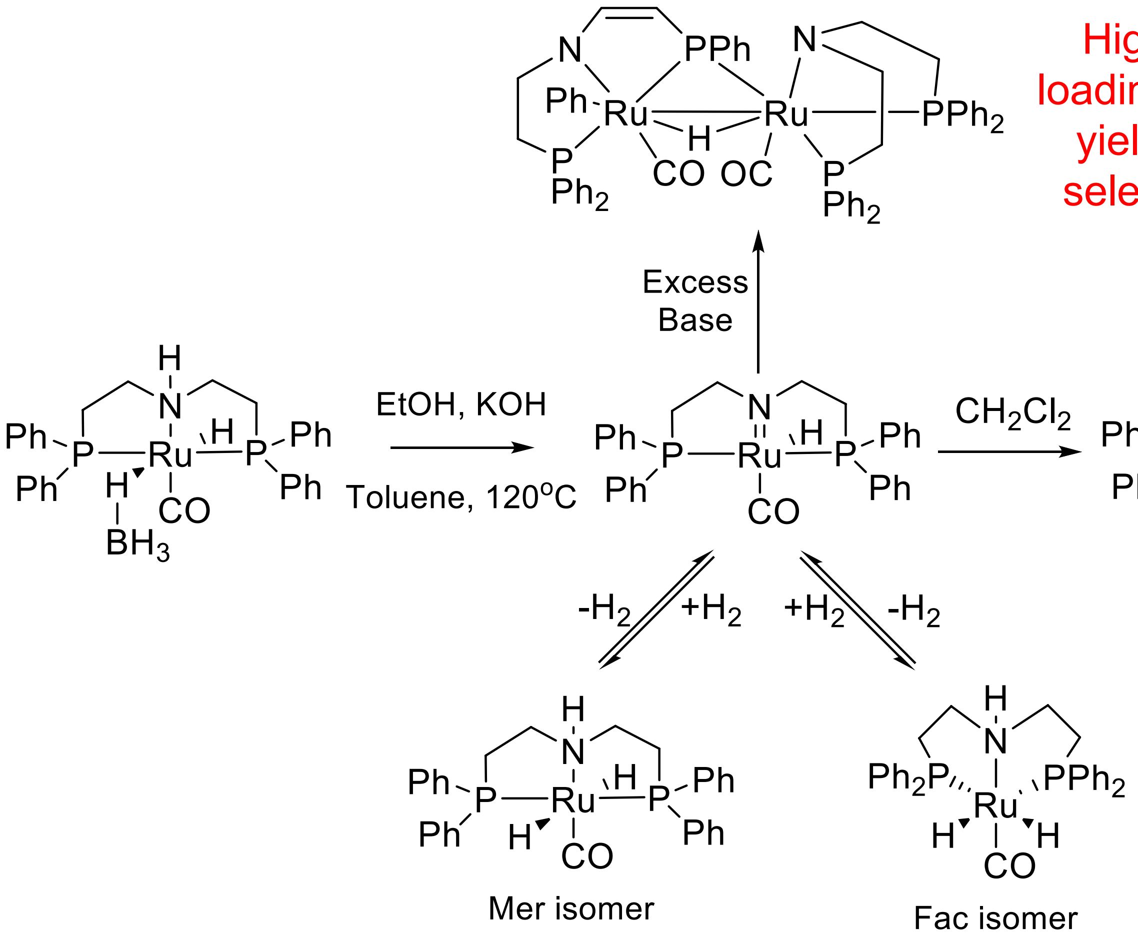
Other products include



1-butanol
Guerbet Product



ethyl acetate
Tishcenko Product

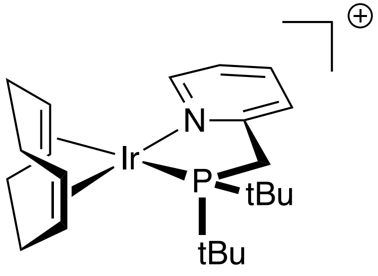


High hydroxide loading leads to low yield (48%) and selectivity (96%).

Progress: Addressing Reviewers' Comments

- This project has never been reviewed and is not scheduled for review in 2024.

- Proposal reviewers criticize our dependance on iridium.
  - While reviewers are right that iridium is a sustainability problem, we submit that high catalyst longevity and efficient catalyst recovery address this issue.
  - Our commercialization teammates at Catapower point out, depending on market conditions, that even with a catalyst as simple as iridium precursor **1**, the ligand costs exceed the iridium costs.



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  - We have transitioned our ethanol-to-acetate chemistry away from iridium to ruthenium to mitigate catalyst cost an improve overall process sustainability.
  - We have reported the first scale-flexible process for recycling iridium-containing waste, primarily comprising iridium used in the development of our H2@Scale project, DE-EE0008825, ca. 5 g of iridium over 4 years. This appeared in *Green Chemistry* in 2024 as an RSC-designated "Hot Paper".

Collaboration and Coordination

- **Core Project Team** meetings will occur bi-weekly among USC, Brookhaven, Los Alamos, and CalState LA investigators. This facilitates student interactions with DOE National Laboratory scientists and staff.

Brookhaven National Laboratory

Los Alamos NATIONAL LABORATORY EST. 1943

- **HyMARC Collaboration** meetings will occur monthly by videoconference among the project team and our HyMARC contact, Hannah Breunig at Lawrence Berkley Lab. This enables the seed project team to remain connected to directions in HyMARC and plan for technology validation and transfer.

HyMARC Hydrogen Materials Advanced Research Consortium

BERKELEY LAB

SEIA/Community Benefits Plan and Activities

- **Advancing Diversity, Equity, Inclusion, and Accessibility.** We subcontract CalState LA, an outstanding primarily minority serving institution (MSI) in Los Angeles that trains undergraduate and masters students, to provide students who will work in the technical aspects of our project, both at CalState and USC. We also engage CalState faculty in regular meetings with HyMARC staff.

- **Energy Equity.** Acetates are highly advantaged fertilizers and soil amendments. One successful our technology will enable production of large supplies of these materials near agricultural communities in the California central valley and the Gulf Coast. As we succeed in providing more of these into underprivileged farming communities, we will provide them with low-cost soil amendments that will both advantage farmers' ability produce products and we will displace chemical fertilizers and pesticides from farmland. This mitigates impacts of eutrophication caused by these materials today, selectively impacting underprivileged communities.

- **Investment in America's Work Force.** We pride ourselves in providing training, particularly at the undergraduate level, to support the development of a clean energy work force. For example, two USC trainees in our current award are underrepresented: (Dr.) Van Do, who developed our CO_2-to-formate preliminary data, went on to a role at the California Energy Commission. AJ Chavez was integrally involved in design and construction of our high pressure formic acid reactor. He went on the graduate studies at the University of California, Santa Barbara in sustainability science.

Remaining Challenges and Barriers

- **Select and Optimize Ethanol-to-Acetate Conditions**
  - We are currently finalizing our first report of the preparative conversion of ethanol to potassium acetate.
  - Following this first report, we will optimize 2-3 catalysts for high yield, selectivity, and turnover at elevated pressure and select a lead system with which to proceed to our continuous operation reactor.

- **Reactor Construction**
  - Design and construction of our continuous operation reactor will commence when DOE funds are received. This effort will be led out of Los Alamos (LANL).

- **Computational Studies on Mechanism and Selectivity**
  - Computational studies will be led out of Brookhaven (BNL) and will commence when DOE funds are received.

Proposed Future Work

- We will execute the project plan and deliverables as originally proposed. No funding has been received for this project at the time of writing.

Any proposed future work is subject to change based on funding levels

Summary

- **We will develop technology to reform ethanol to potassium acetate and hydrogen**
  - Acetate salts are valuable as agrochemicals; this value subsidizes the production of hydrogen and drives down its net price. The same argument holds for glycerol to lactate, with higher value and lower market cap.
  - Whereas the hydrogen market is larger than the acetate or lactate market, we imagine that the ethanol technology will complement other hydrogen carriers, eg. formic acid or water electrolysis, to subsidize value and push down the net cost of hydrogen production.

- **We're excited to get going!** While we're not yet funded (at time of writing), we've made important inroads toward establishing feasibility of our plan.
  - We have identified a ruthenium system, RuMACHO-BH, for acetate production and identified conditions for both ambient and self-pressurizing reactions.
  - We have developed a cost of production model showing that the value-added coproduct of H_2 production makes ethanol an industrially relevant one-way hydrogen carrier without the need for government subsides.