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Ru-based homogeneous and heterogeneous catalysts for ethylene glycol (de)hydrogenation

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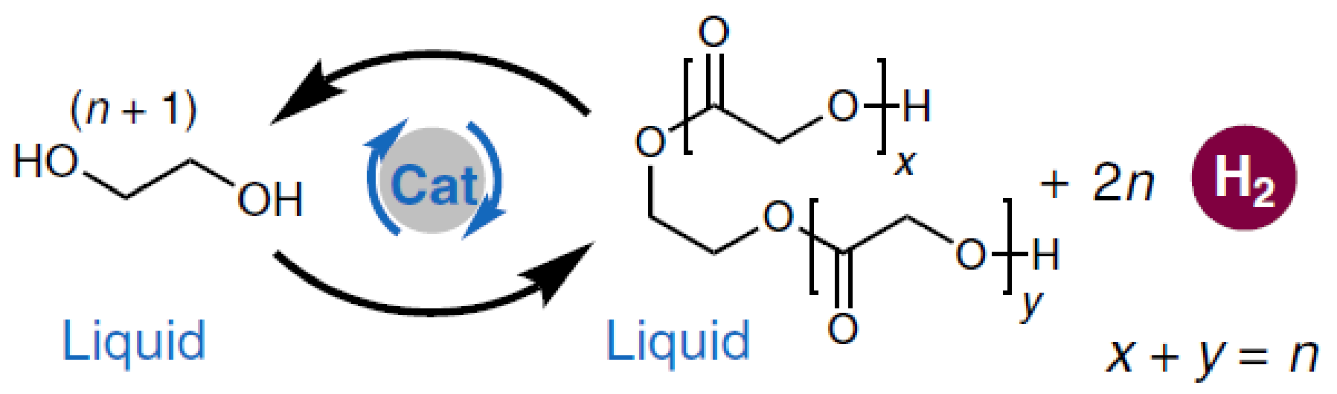
Overview

Hydrogen is valued as a clean source of energy, but storage and transport of hydrogen in its gas form is a challenge due to low energy density and safety issues. Liquid organic hydrogen carriers (LOHCs) are organic compounds with covalently bonded hydrogen that can act as hydrogen batteries for long-term hydrogen storage since they can be catalytically dehydrogenated and hydrogenated. Ideal LOHCs should be able to be easily transported, reversibly bond to hydrogen, and integrate with current liquid fuel infrastructure. Catalysts for LOHC cycling should have favorable thermodynamic conditions, and ruthenium catalysts are good candidates. As part of the HyMARC effort (www.hymarc.org), we are investigating reversible hydrogen storage in LOHCs based on aliphatic polyalcohols. Here, we present results of reversible dehydrogenation of ethylene glycol in the presence of homogeneous and heterogeneous ruthenium catalysts with pincer-type ligands.

Objective: To heterogenize *Ru-catalysts with a silica support to improve the dehydrogenation and hydrogenation of hydrogen from ethylene glycol.*

Reaction scheme



- HSC: 6.5 wt% (maximum)

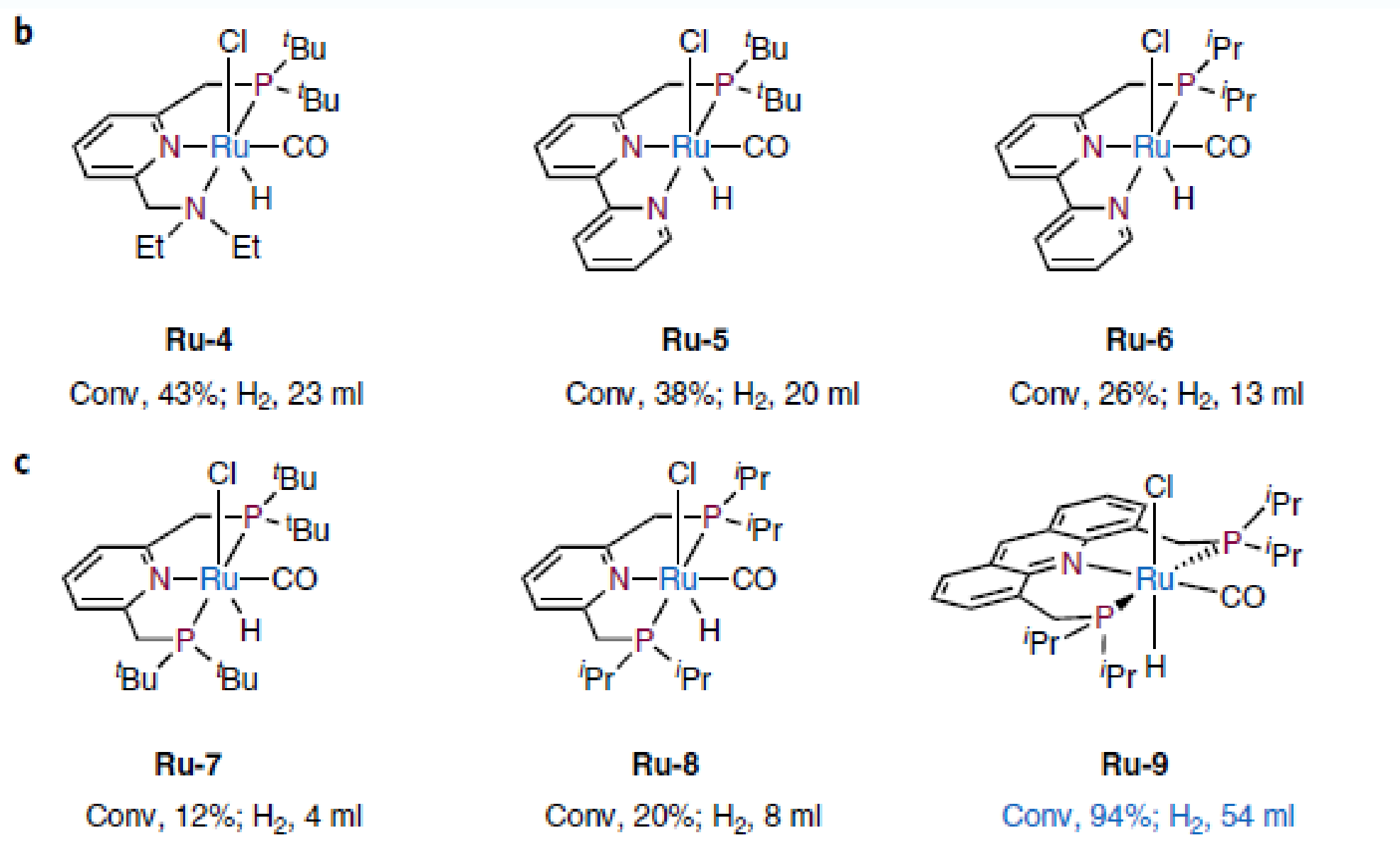
- Inexpensive
- Reversible
- Convenient

Ethylene glycol (EG) is renewable and inexpensive and theoretically has a hydrogen storage capacity of 6.5 wt%. The liquid to liquid dehydrogenation of EG is catalyzed by a Ru-catalyst, and the product is a polymer of EG with varied lengths. And depending on number of polymer units, this reaction has a hydrogen storage capacity from 3.25 to 6.5 wt%. Furthermore, this reaction is reversible, as the ester oligomer will decompose into ethylene glycol after a hydrogenation reaction with the same Ru-catalyst.

1. Zou, Y. Q.; von Wolff, N.; Anaby, A.; Xie, Y.; Milstein, D., Ethylene Glycol as an Efficient and Reversible Liquid Organic Hydrogen Carrier. *Nat Catal* **2019,** *2* (5), 415-422.

State-of-the-art Ru-catalysts

Professor David Milstein's group published a series of ruthenium pincer complexes that catalyze reversible hydrogen storage using various LOHCs, including ethylene glycol. The catalyst is typically activated by the removal of the Cl ligand with a base. We chose these catalysts because they are well studied and are commercially available.



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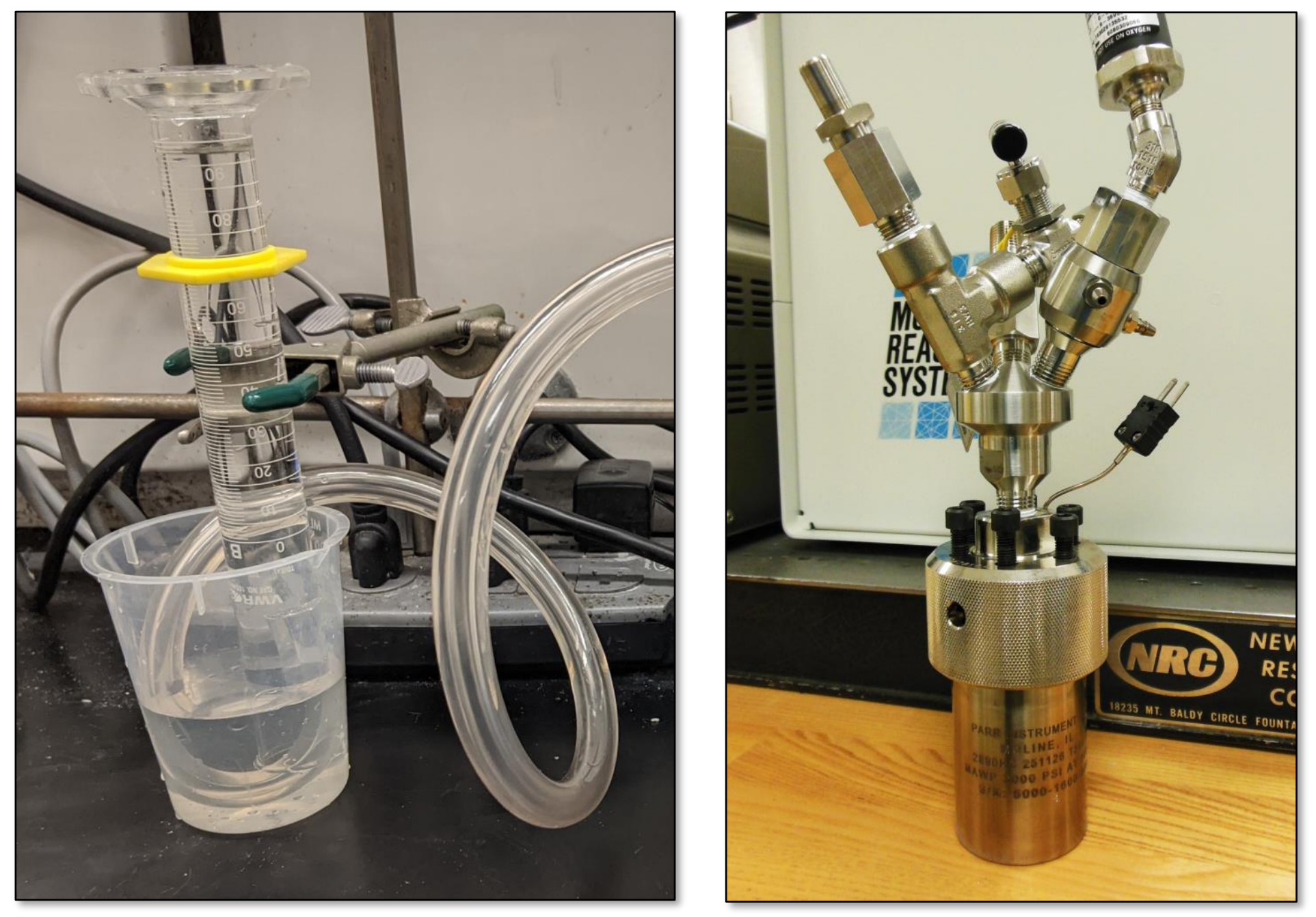
Experimental setup

The reaction is carried out in an Parr bomb autoclave to prevent hydrogen gas from escaping.

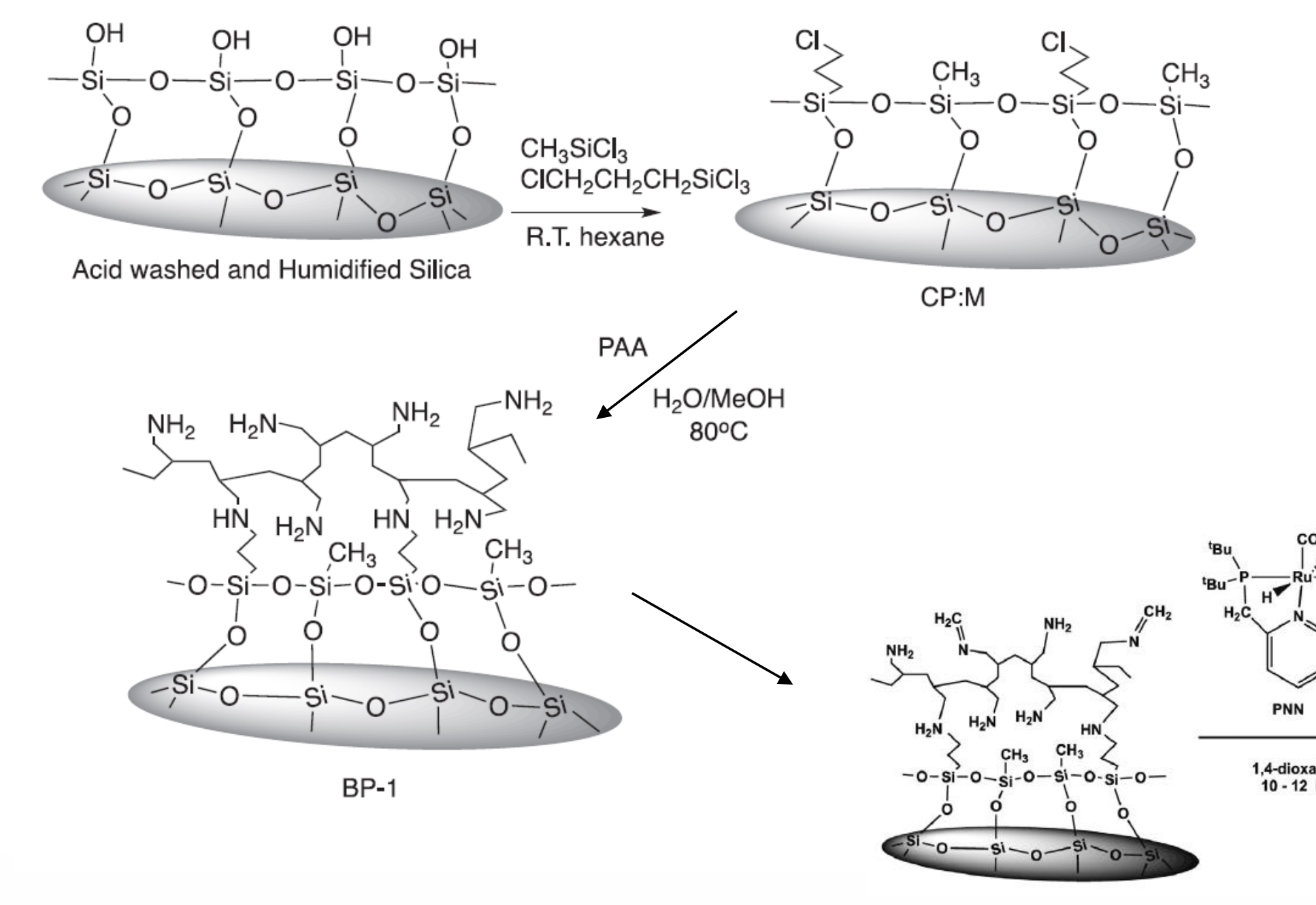
Dehydrogenation conditions: 0.02 mmol catalyst, 0.04 mmol tBuOK, 2 mmol EG. For reactions with solvent: 1 mL toluene, 1 mL DME. The forward reaction was carried out over 72 hours at 150 °C, with gas collection at 24 hour timepoints.

Hydrogenation conditions: 40 bar hydrogen gas at 150 °C for 48 hrs. Afterwards, the Parr bomb was charged with hydrogen to regenerate the starting materials.

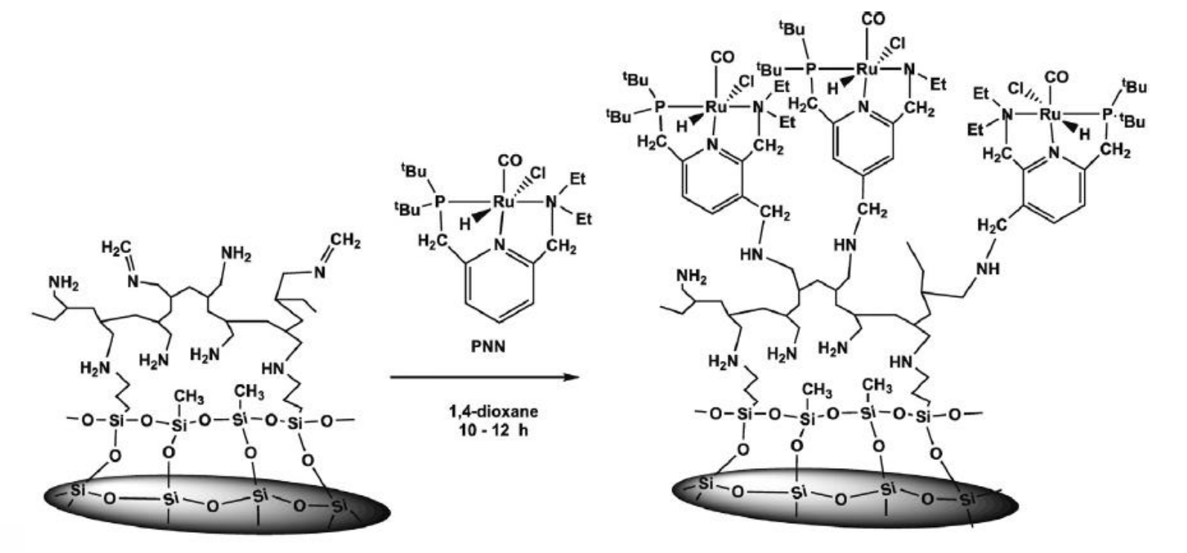
Parr bomb setup



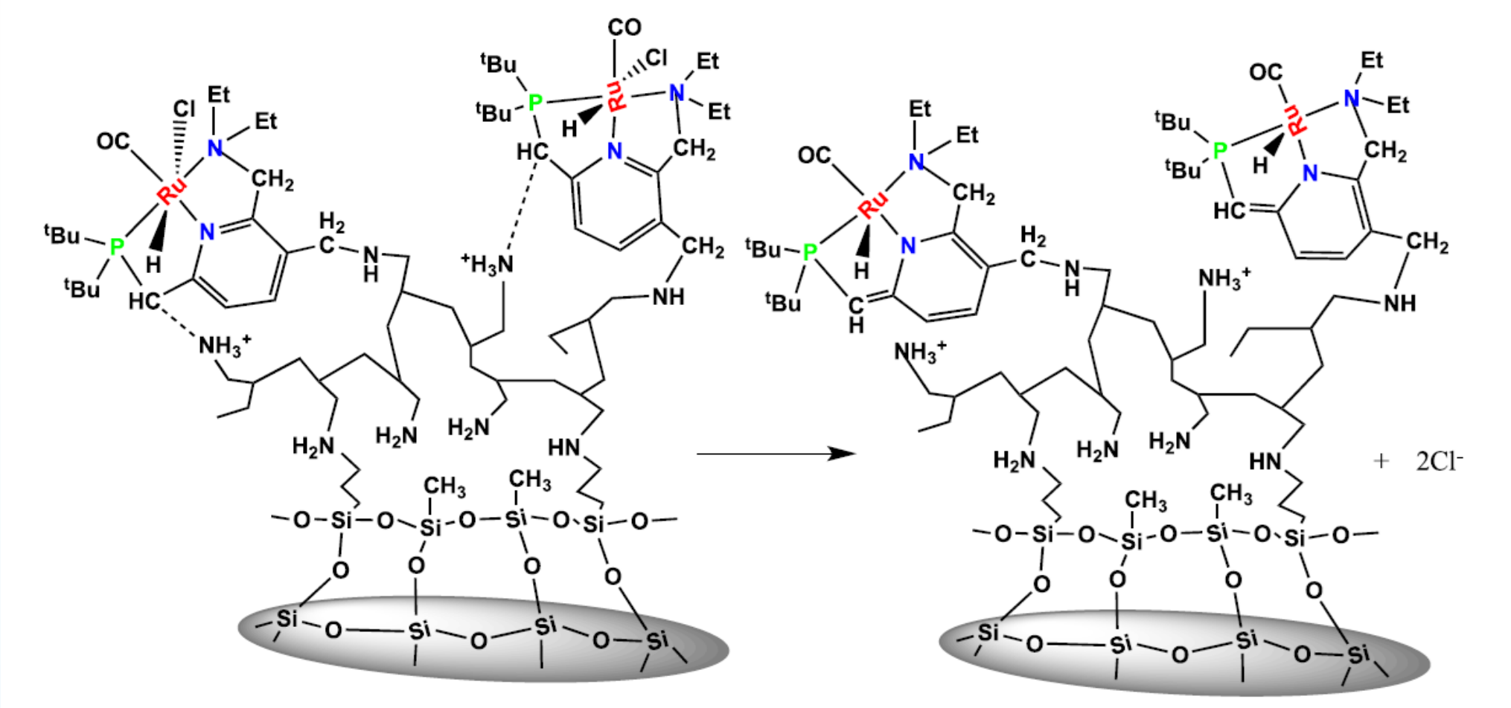
Ru-MACHO and silica supports

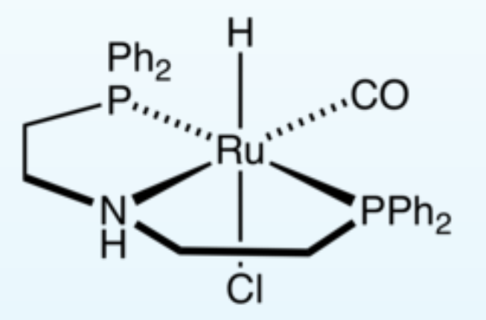


Heterogeneous catalysts are typically less active than homogenous catalysts, so we aim to anchor Ru-catalysts to silica without loss of reactivity.



We used procedures published by Goni et al. to anchor Ru-4 on silica (Ru-4 @ SBA-15) through a Mannich reaction. This heterogenized catalyst could activate and generate hydrogen gas without the addition of base. We hypothesize this is due to unanchored amine groups.





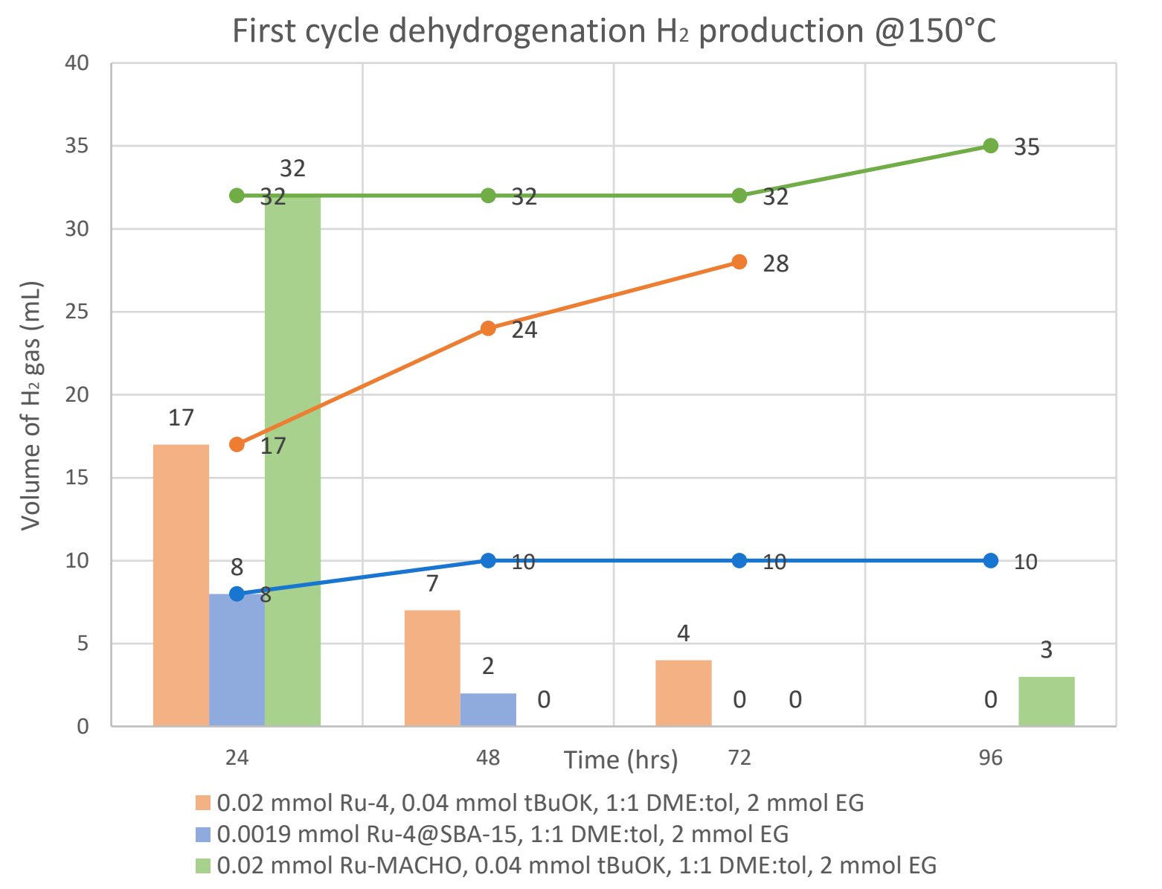
Ru-Macho is a commercialized Ru-catalyst that in inexpensive in comparison to Milstein's catalysts. It has a similar structure, with Ru-N and Ru-H bonds, which have been reported to be essential to the mechanism of the dehydrogenation reaction.

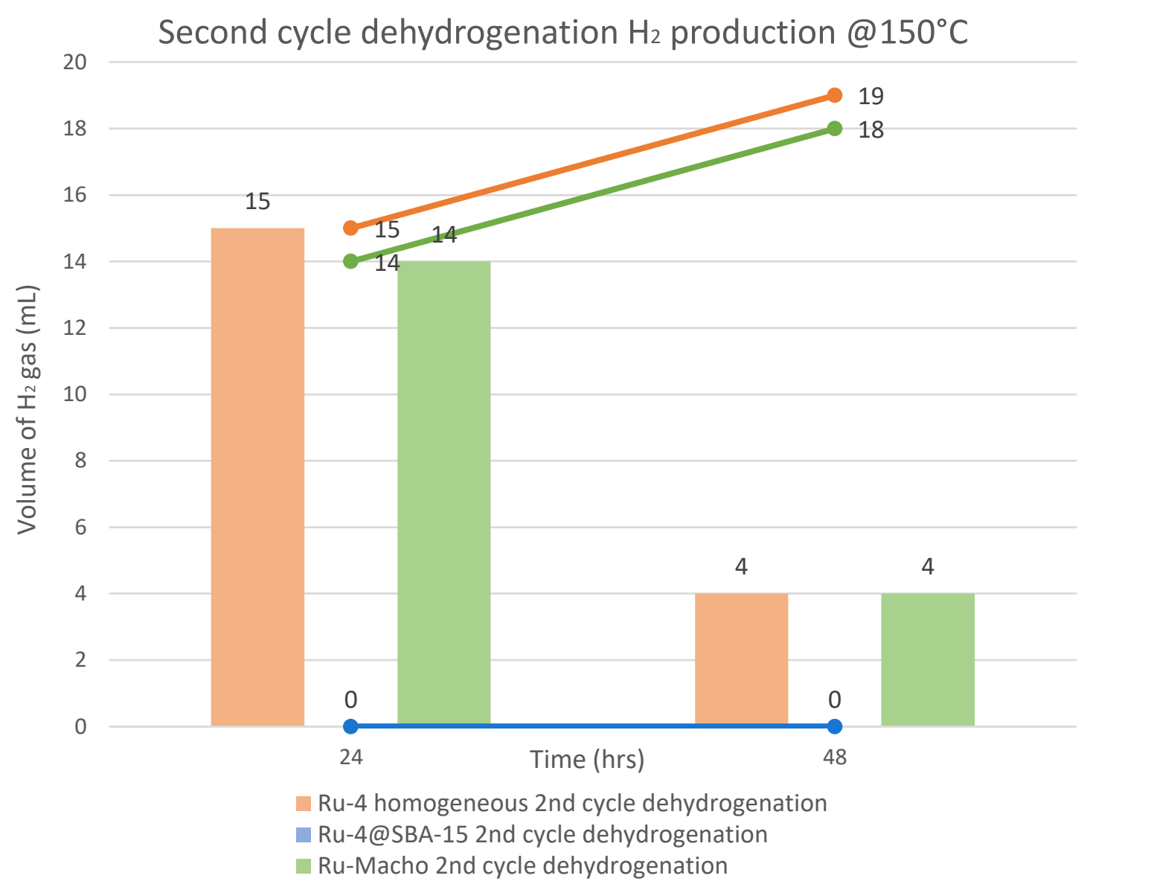
Hughes, Structural Investigations of Silica Polyamine Composites: Surface Coverage, Metal Ion Coordination, and Ligand Modification. *Ind. Eng. Chem. Res.* **2006,** (45, 6538-6547).

Goni, M. A.; Rosenberg, E.; Gobetto, R.; Chierotti, M., Dehydrogenative coupling of alcohols to esters on a silica polyamine composite by immobilized PNN and PONOP pincer complexes of ruthenium. *Journal of Organometallic Chemistry* **2017,** *845*, 213-228.

Pham, J.; Jarczyk, C. E.; Reynolds, E. F.; Kelly, S. E.; Kim, T.; He, T.; Keith, J. M.; Chianese, A. R., The key role of the latent N–H group in Milstein's catalyst for ester hydrogenation. *Chemical Science* **2021,** *12* (24), 8477-8492.

Data collection and preliminary results

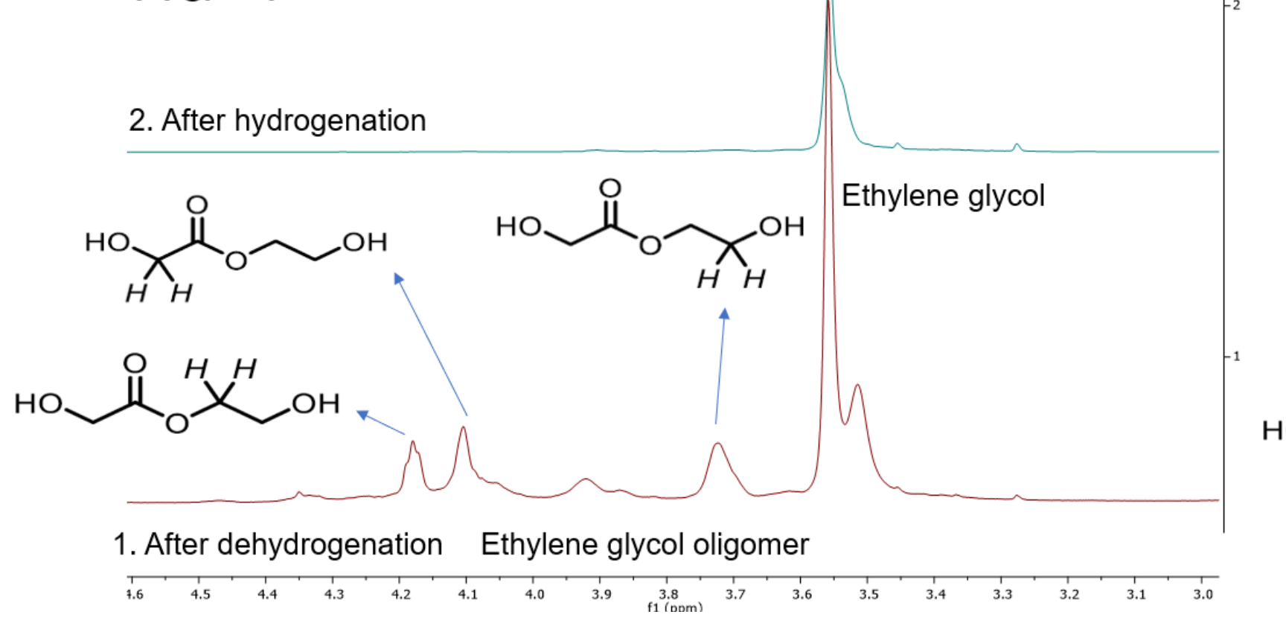




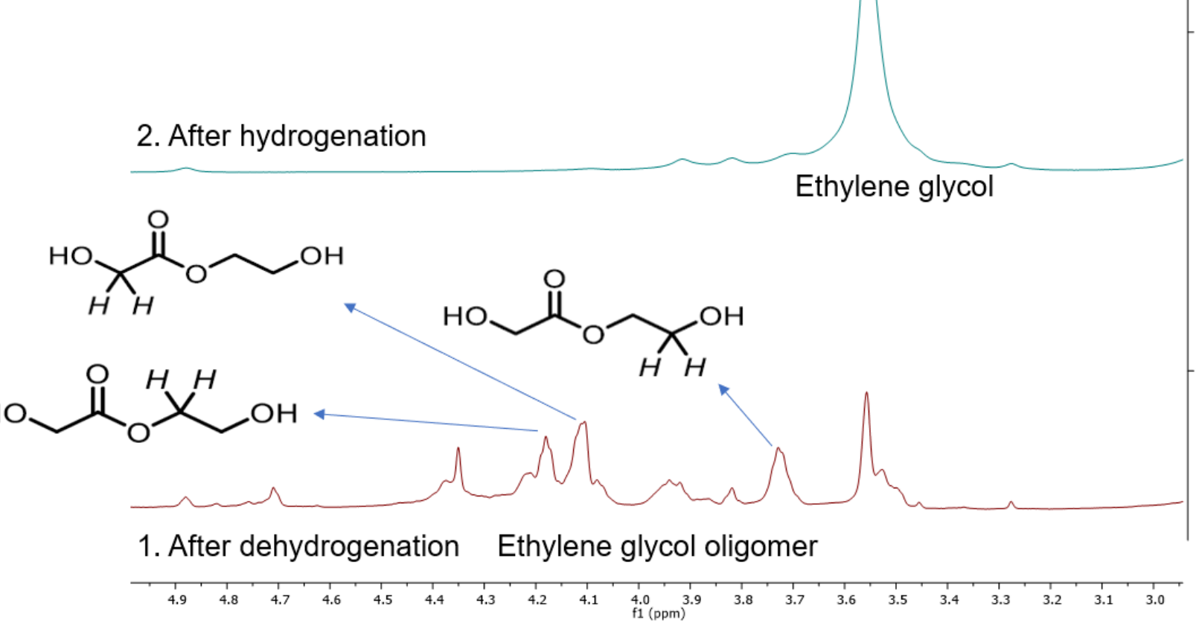
Ru-4 homogeneous catalyst was our base line to repeat Milstein's experiment (34 mL of H_2 with 43% conversion). We successfully produced 28 mL of H_2 with 46% conversion. Ru-4 @ SBA-15 produced the least gas. Ru-Macho produced the most gas in 24 hrs and the most gas overall.

NMR characterization

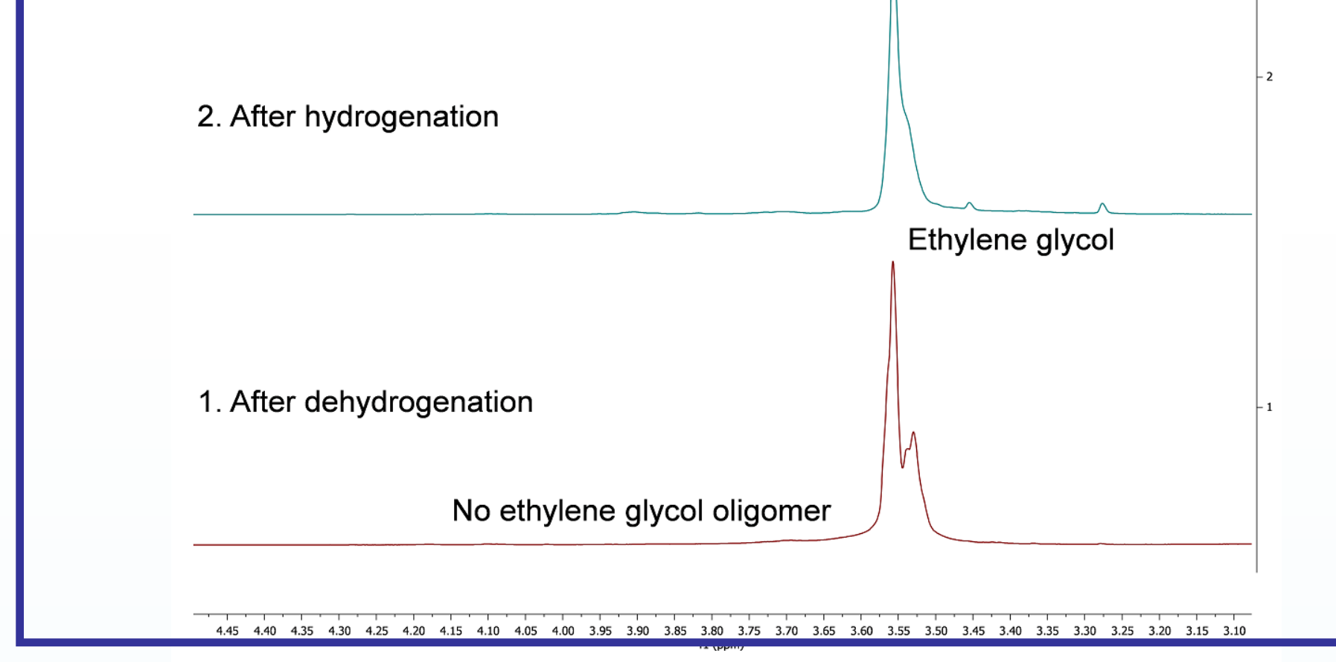
Ru-4



Ru-Macho



Ru-4@SBA-15



Nuclear Magnetic Resonance (NMR) spectra were collected after the catalytic dehydrogenation reaction (bottom spectra), as well as after the hydrogenation reaction (top spectra). Our results indicate that Ru-4 and Ru-Macho are efficient in regenerating ethylene glycol under hydrogen, whereas the anchored Ru-4@SBA-15 only catalyzes the dehydrogenation reaction.

Summary and conclusions

- We showed that both homogenous and heterogenous Ru pincer catalysts efficiently generate H_2 from EG.
- Our NMR data indicates anchored Ru-4 @ SBA-15 cannot regenerate EG under hydrogen pressure.
- Future experiments are planned using a high-throughput Parr reactor to probe the origin of catalytic activity and mitigate the deactivation of the heterogeneous catalyst.
- We will also plan to mount the most active catalyst, Ru-Macho, on silica, with the goal of making a more efficient H_2 cycling catalyst

Acknowledgements

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