Toward Sustainable Chemicals and Fuels: Catalytic Conversion of Biomass Polyols to Olefins

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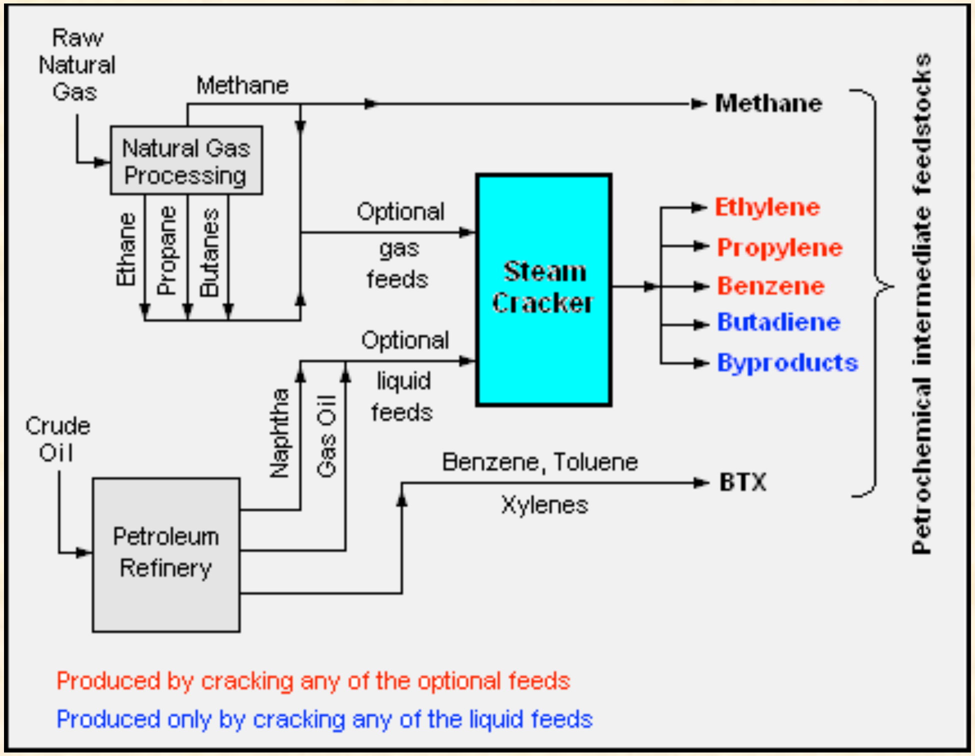
Hydrocarbon Production from Fossil Resources

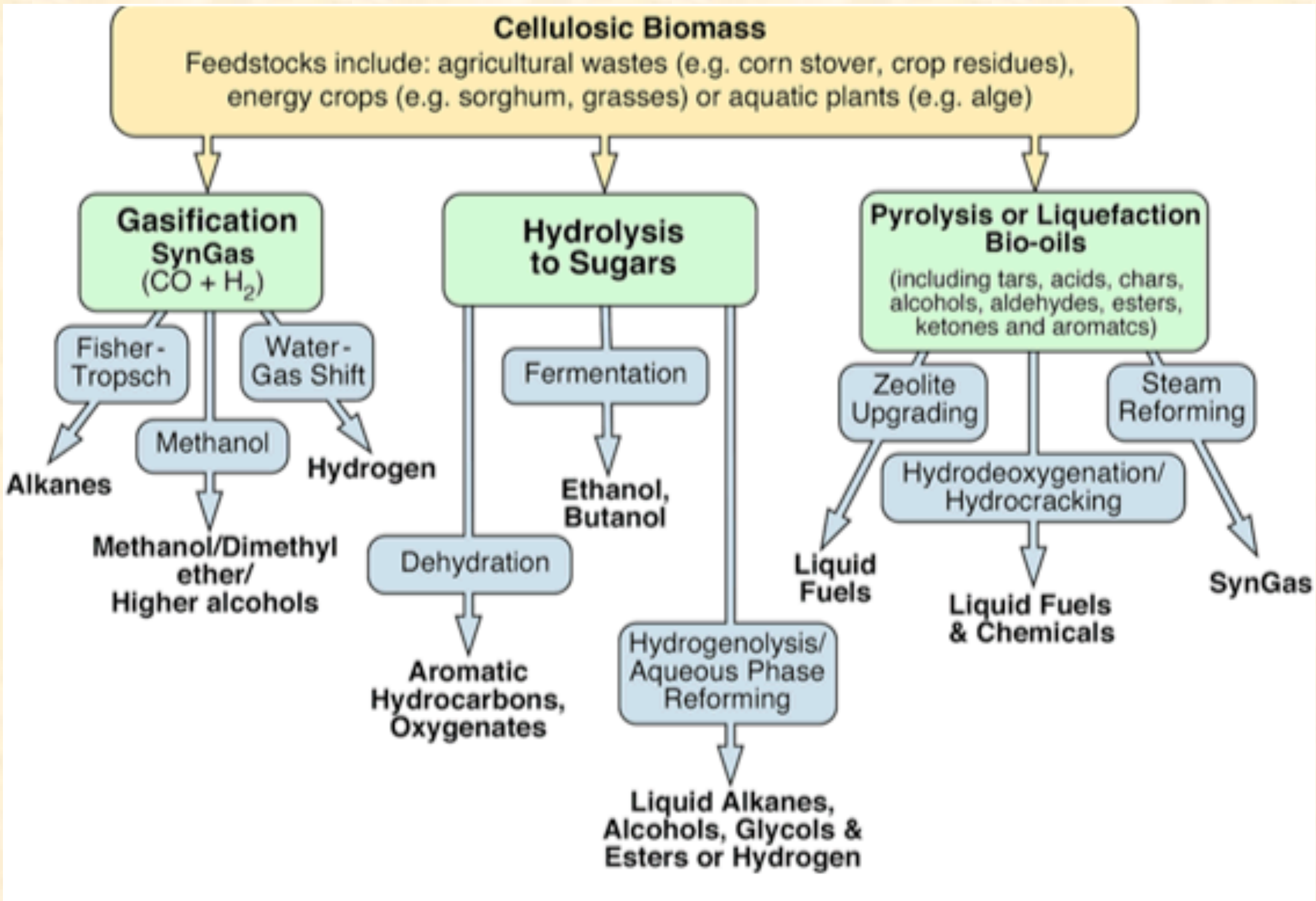
$(CH_2)_n$, $(CH)_n$

aliphatics, aromatics



Fuels and Chemicals from Cellulosic Biomass

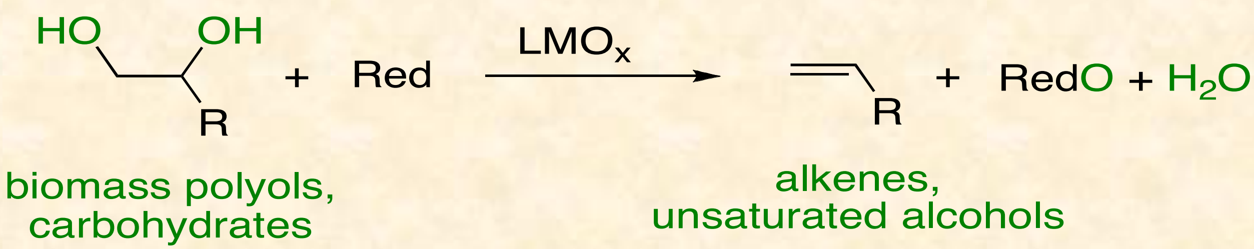
$C_n(H_2O)_n$



Deoxydehydration of Polyols (DODH)

To convert abundant and renewable hydroxyl-rich biomass components into useful chemicals or fuels, selective processes are needed to remove some/all of the oxygens.

Deoxydehydration of Polyols

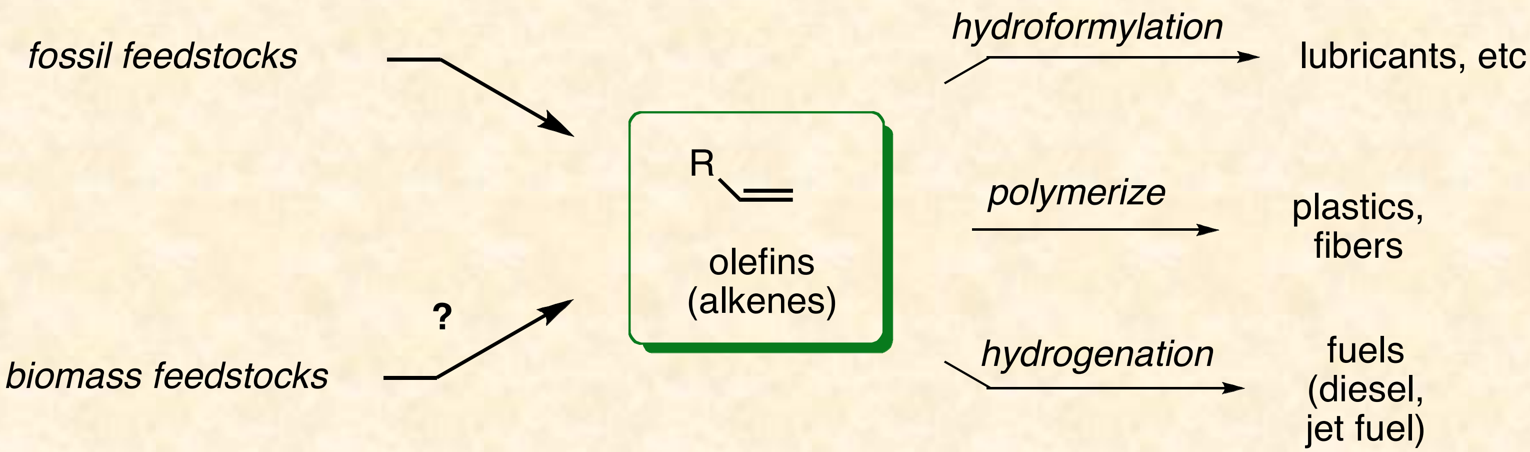


Red = reductant; e.g. SO_3^{2-}, H_2; RedO = SO_4^{2-}, H_2O

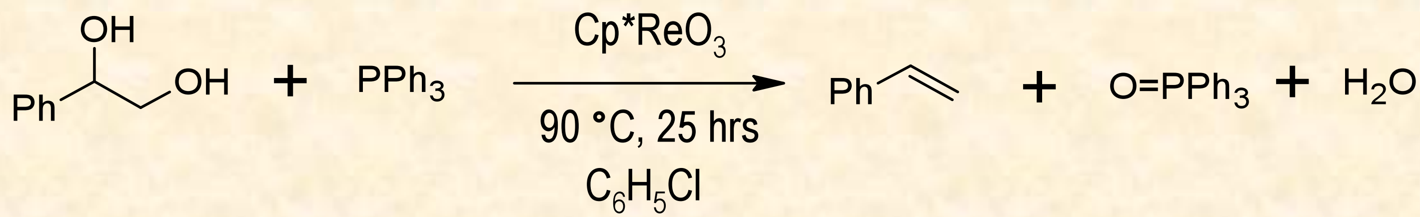
DODH features:

- replaces 2 -OH with C=C
- requires a reducing agent (Red) and a catalyst
- produces higher energy, useful products
- requires selective –OH activation/removal by the catalyst

Olefins are valuable chemical intermediates and products



Prior/Recent Re-catalyzed DODH systems



G. Cook and M. Andrews, *J. Am. Chem. Soc.* **1996**, 118, 9448.

Concurrent with our group's work:

- $MeReO_3$ (cat) + H_2 (RA)

M. Abu-Omar et al. (Purdue)*, Inorg. Chem.* **2009**, *48*, 9998.

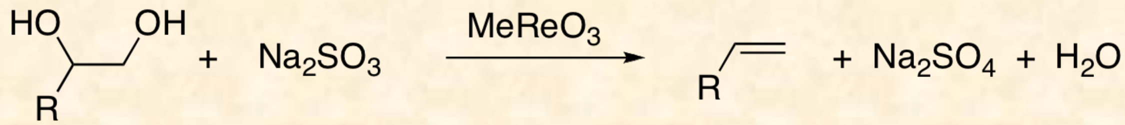
- $Re_2(CO)_{10}$/air + alcohol (RA)

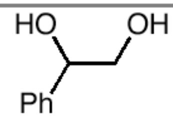
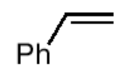
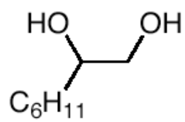
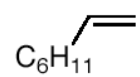
R.G. Bergman et al (U.C. Berkeley)*, J. Am. Chem. Soc*. **2010**, *132*, 11404.

Potential Reductants for Polyol DODH

Reductant	Product	ΔH° for DODH (kcal/mol)	Cost/mol
PPh_3	$OPPh_3$	- 17	\$ 5.0
H_2	H_2O	- 14	\$ 0.01-.10
CO	CO_2	- 15	\$ 0.10-.50
Na_2SO_3	Na_2SO_4	- 13	\$ 0.10

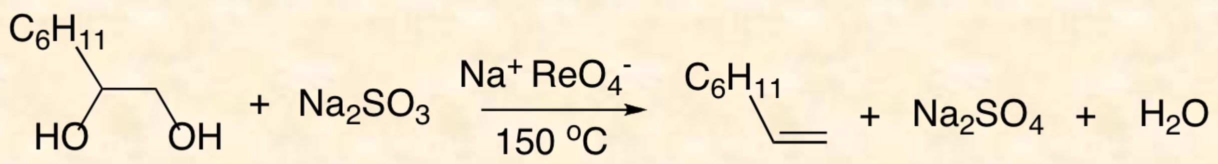
$MeReO_3$ Catalyzes DODH by Sulfite Salts

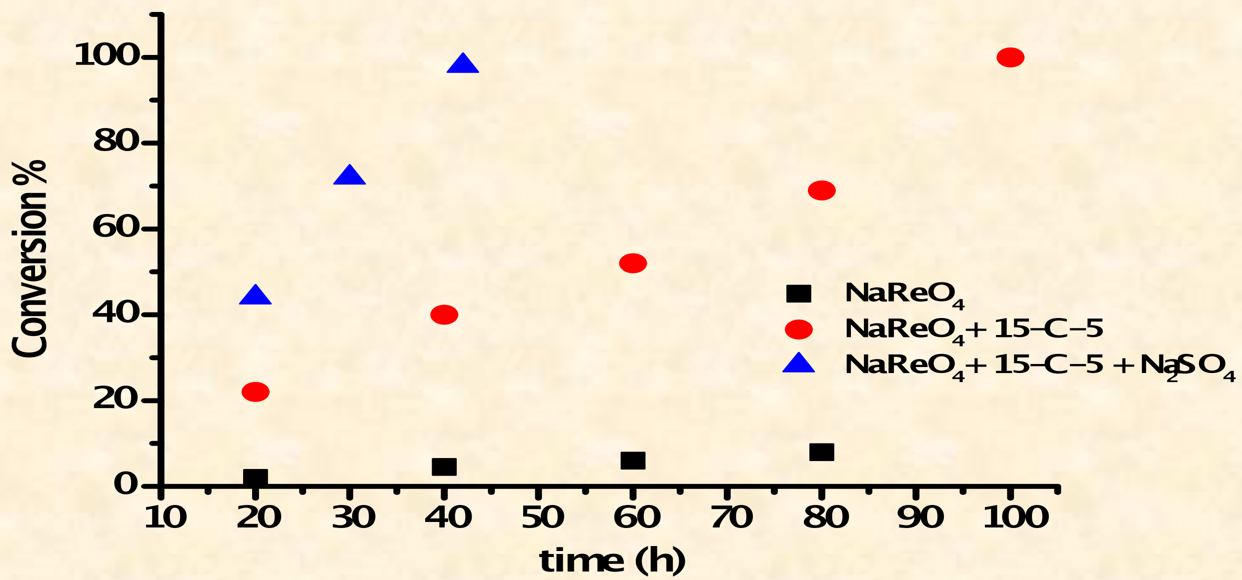


entry	substrate	Catalyst (mol%)	solvent/ additive	major product	time (h)	% conv.	% yield[a]
1	 (0.2 M)	$MeReO_3$(10)	benzene		4	100	59
2		(8)	benzene		4	100	59
3		(5)	THF		72	25	15
4		(5)	CH_3CN		96	30	15
5		(8)	benzene		168	95	34
6		(8)	PhCl		40	100	45
7		(8)	PhCl, 15-crown-5		21	98	43
8		(2)	none		20	75	60

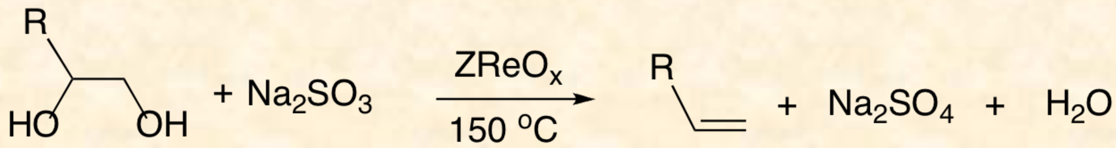
S. Vkuturi, G. Chapman, I. Ahmad, K.M. Nicholas, *Inorg. Chem.* **2010,** *49*, 4744.

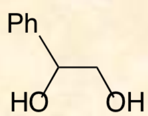
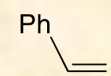
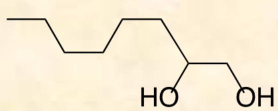
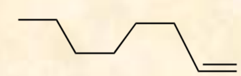
$Z^+ ReO_4^-$ also catalyzes DODH; additives enhance conversion rate



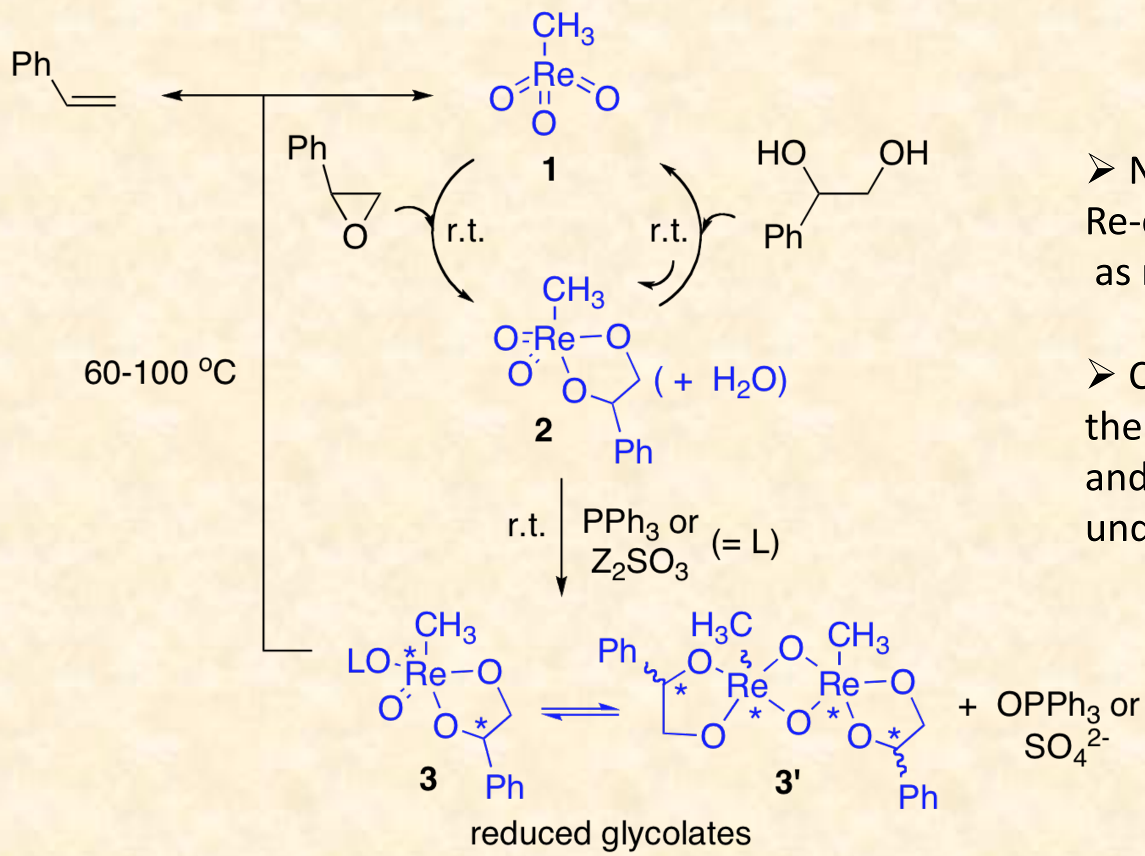


Substrate, catalyst effects on $Z^+ReO_4^-$ DODH



Substrate	Catalyst	t (h)	Conv.[b] %	Yield %	Major product
	$NaReO_4$	40	100	53	
	NH_4ReO_4	12	100	34	
	Bu_4NReO_4	59	100	71	
	Re_2O_7	63	80	23	
	$NaReO_4$	42	98	38	
	NH_4ReO_4	26	100	37	
	Bu_4NReO_4	100	100	68	

Detection of reactive intermediates

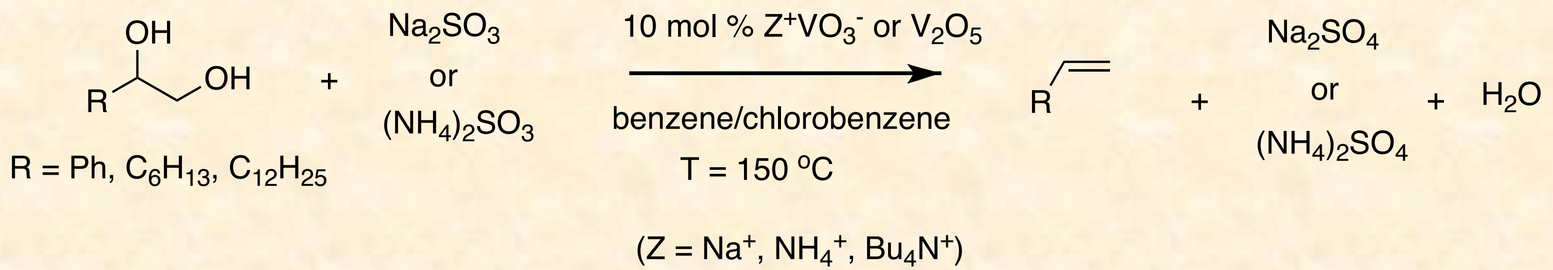


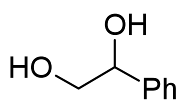
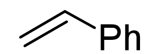
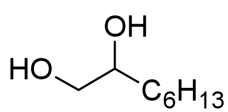
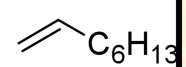
- NMR and IR studies detect Re-compounds **2** and **3** as reaction intermediates.

- Computational modeling of the reaction intermediates and transition states is underway.

I. Ahmad, G. Chapman, K.M. Nicholas, *Organometallics*, **2011**, *30*, 2810.

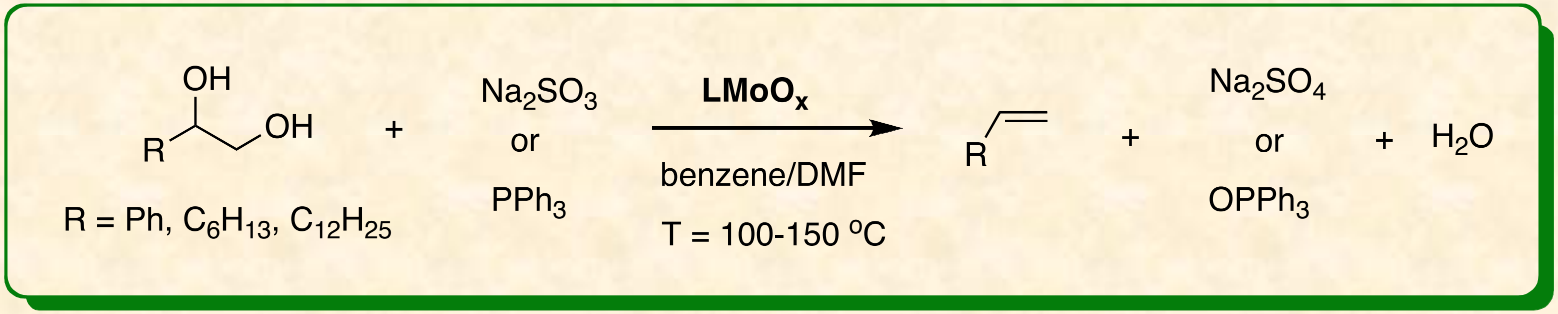
Toward cheaper, more efficient catalysts: Vanadium



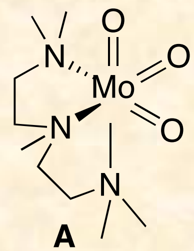
Substrate	Catalyst	t (h)	Conv. %	Yield %	Major product
	$NaVO_3$	84	90	36	
	NH_4VO_3	84	99	43	
	Bu_4NVO_3	39.5	98	33	
	V_2O_5	63	80	23	
	$NaVO_3$	72	45	7	
	NH_4VO_3	72	38	9	
	Bu_4NVO_3	36	45	8	

Garry Chapmann, EPSCOR GRA, unpublished results, 2011-12.

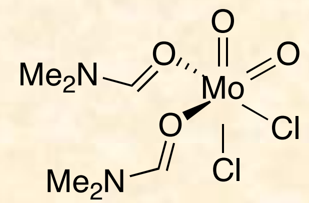
Toward cheaper, more efficient catalysts: Molybdenum



$LMoO_x$ = $(NH_4)_6Mo_7O_{24}$, $(Bu_4N)_2[Mo_6O_{19}]$, $(Bu_4N)_3[Mo_{12}O_{40}]$,



A



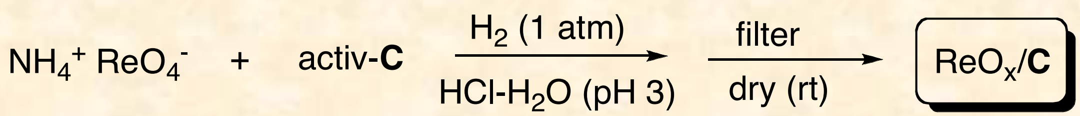
B

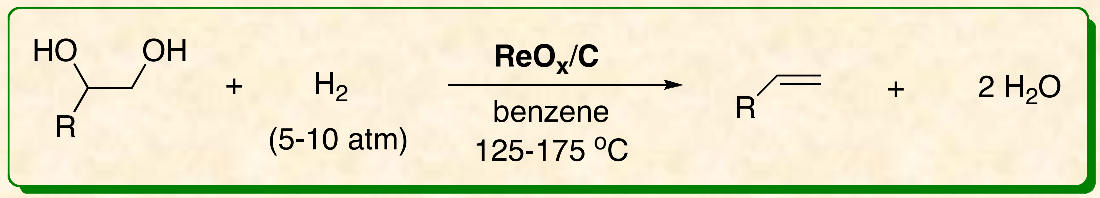
Catalyst (mol%)	Reductant (mmol)	Temp. (°C)	Time (h)	Conversion (% approx)	Alkene Yield (%)
$(NH_4)_6Mo_7O_{24}$ (10)	Sulfite	150	53	85	18
$MoO_2Cl_2(DMF)_2$ (3)	Sulfite	150	24	100	17
$(NH_4)_6Mo_7O_{24}$ (10)	PPh_3	150	48	100	30
$MoO_2Cl_2(DMF)_2$ (3)	PPh_3	100	3	100	33

Dr. Sanjeev Maradur, 2012.

Toward practical *heterogeneous* DODH catalysts

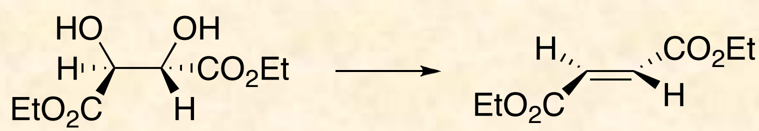
A joint-project with F. Jentoft (O.U. CBME) provides a proof-of-concept:





Catalyst	Time (hr)	Tetradecene (%)
fresh (4 % Re)	25	12
	48	23
	72	42
filtrate + glycol	72	43

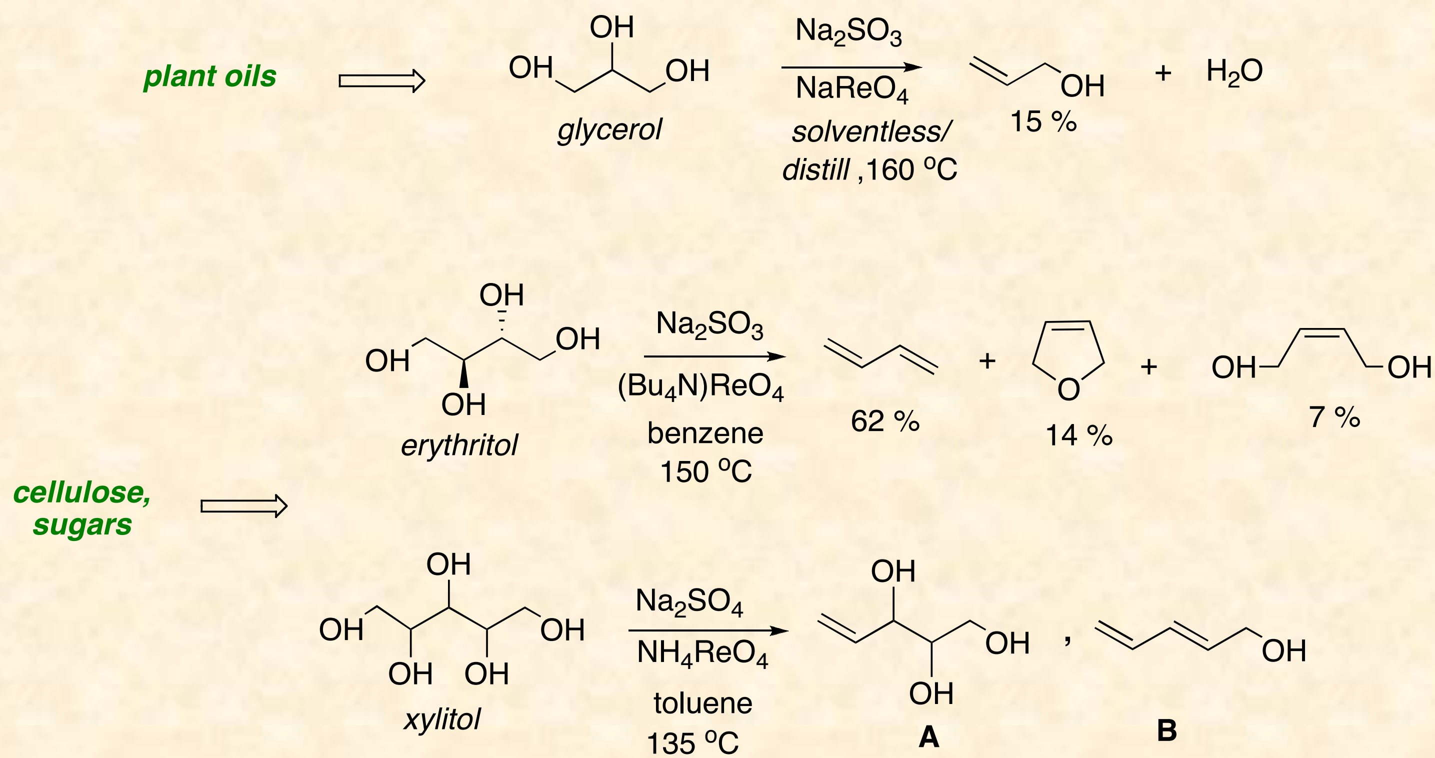
- little/no alkane formed
- catalyst recycling shows 50% decrease in activity after 4 reuses



only isomer !

Alana Denning, EPSCOR-UGRA, 2011-2.

Biomass feedstocks to value-added products



1:1 Xyl/SO_3^{2-} **A** (20 % yield) >> **B**

1:2 Xyl/SO_3^{2-} **B** (40 % yield) >> **A**

Dr. Irshad Ahmad (2011), Camille-Boucher-Jacobs (2012)

Acknowledgements: People

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