Catalysis: Elucidating kinetics and trends using DFT and experiments

Steven Nystrom

Committee:

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Motivation

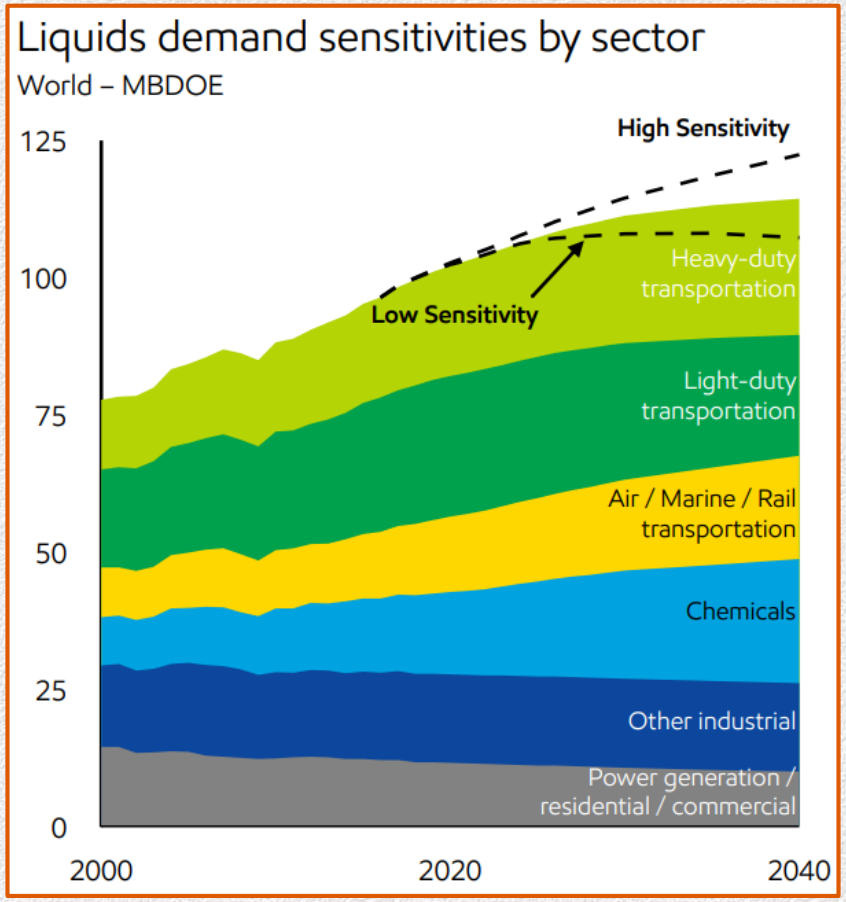
Produce more chemicals and fuels

Using less energy

Carbon neutral way

Reduce emissions and pollution

Catalyst can solve these issues



Catalysts

Produce more chemicals and fuels

Using less energy

Carbon neutral way

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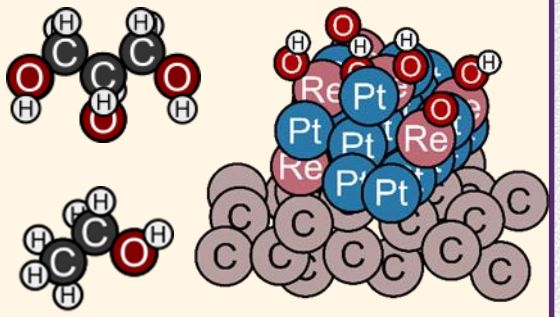
Catalyst can solve these issues

Alcohols on metals

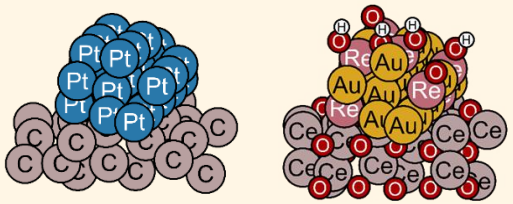


Alcohol hydrogenolysis

Metals:
Pt good at hydrogenation

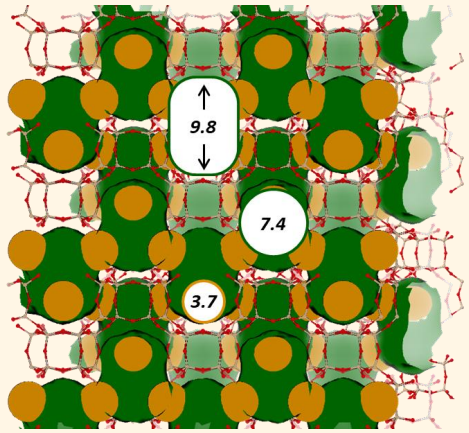
ReO_x acts Brønsted acid

Au poor at hydrogenation



Alcohols in zeolites

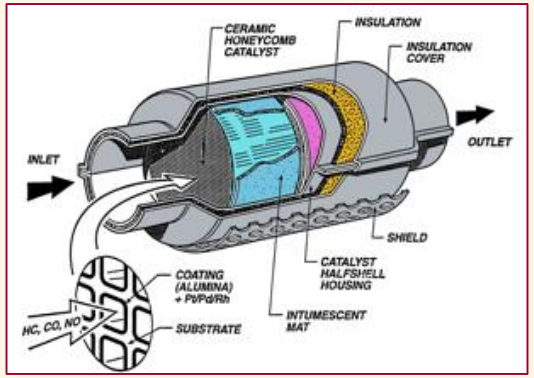
Aluminosilicates (Confinement)



Methanol dehydration

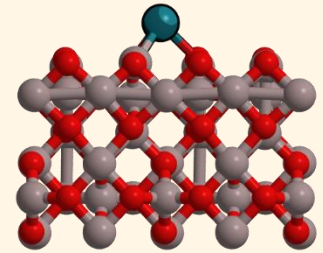
Brønsted acids

Emission control (3-way catalytic converter)



Metals:
Pt, Pd, Rh

Suffer at start up (low T.)

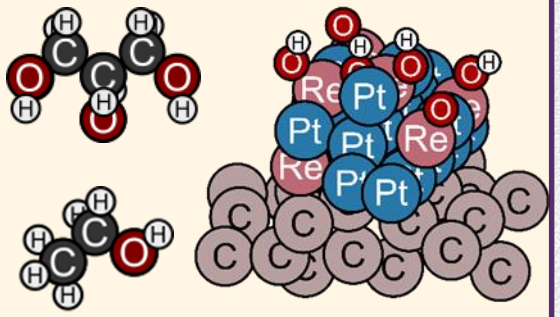


Atomic Rh

Catalytic converter image: meca.org

ReOx promotional effects

Alcohols on metals



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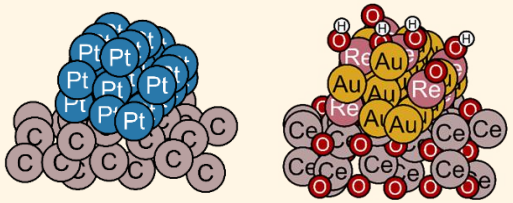
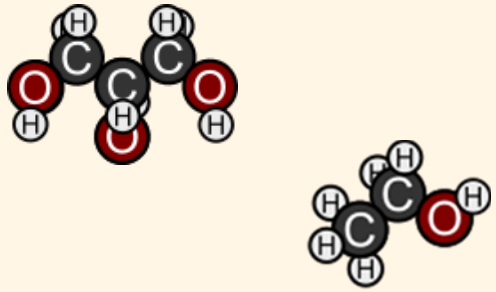


Biomass conversion



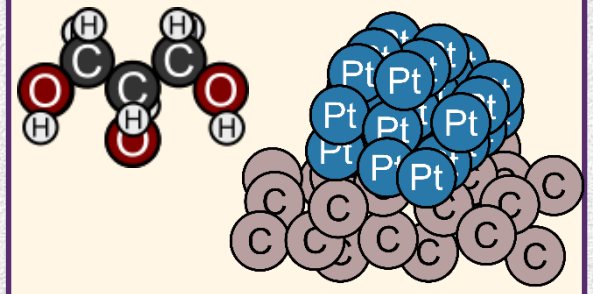
Excess/Waste

Convert to market value chemicals

Requires knowledge of C–O and C–C (hydrogenolysis)

Hydrogenolysis of alcohols

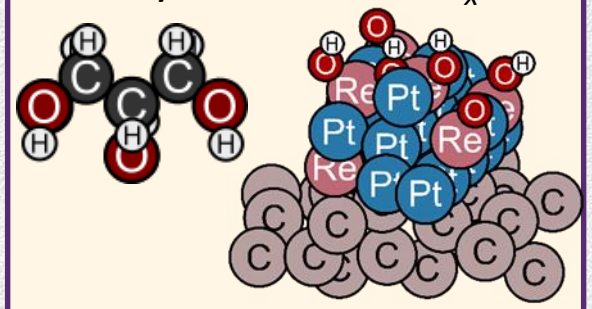
Glycerol on Pt



Glycerol
C–C bonds
Primary C–O
Secondary C–O

Pt well studied hydrogenolysis catalyst

Glycerol on $PtReO_x$

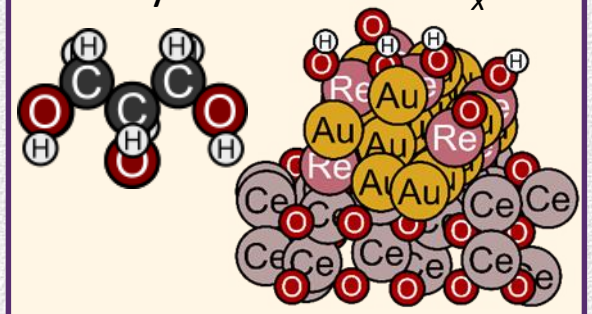


Increases reaction rates

Enhances C–O cleavage

Brønsted acid

Glycerol on $AuReO_x$

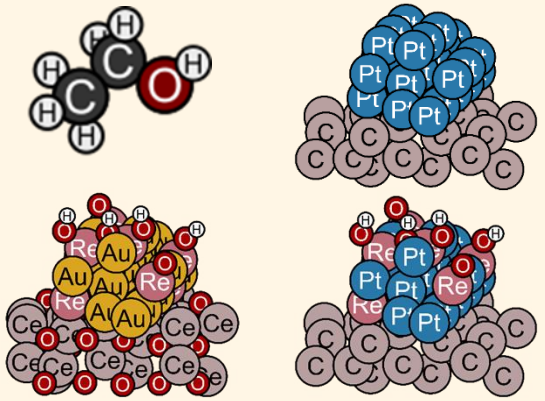


Poor hydrogenation cat.

Unsaturated Products

Help identify intermediates

Ethanol



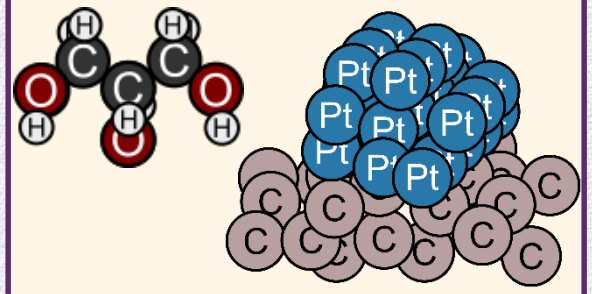
Ethanol
C–C bonds
Primary C–O
Volatile

Ideal for gas phase reaction

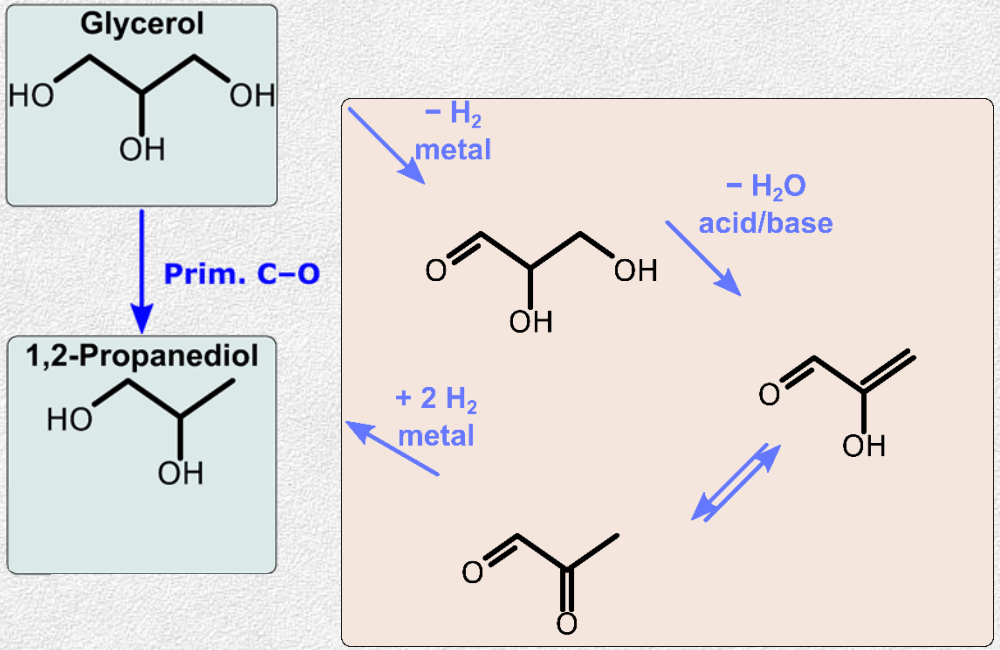
Test effects of water

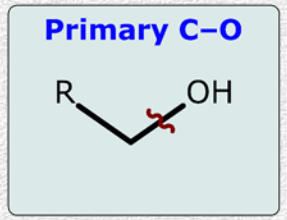
Hydrogenolysis…glycerol on Pt

Glycerol on Pt



1,2-Propanediol

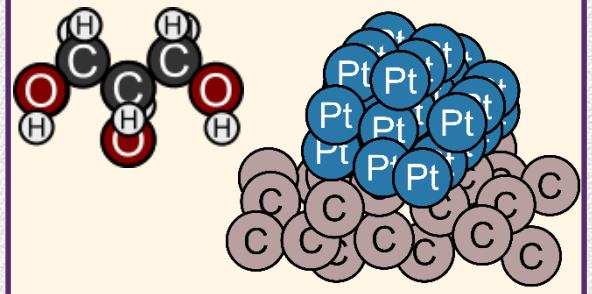




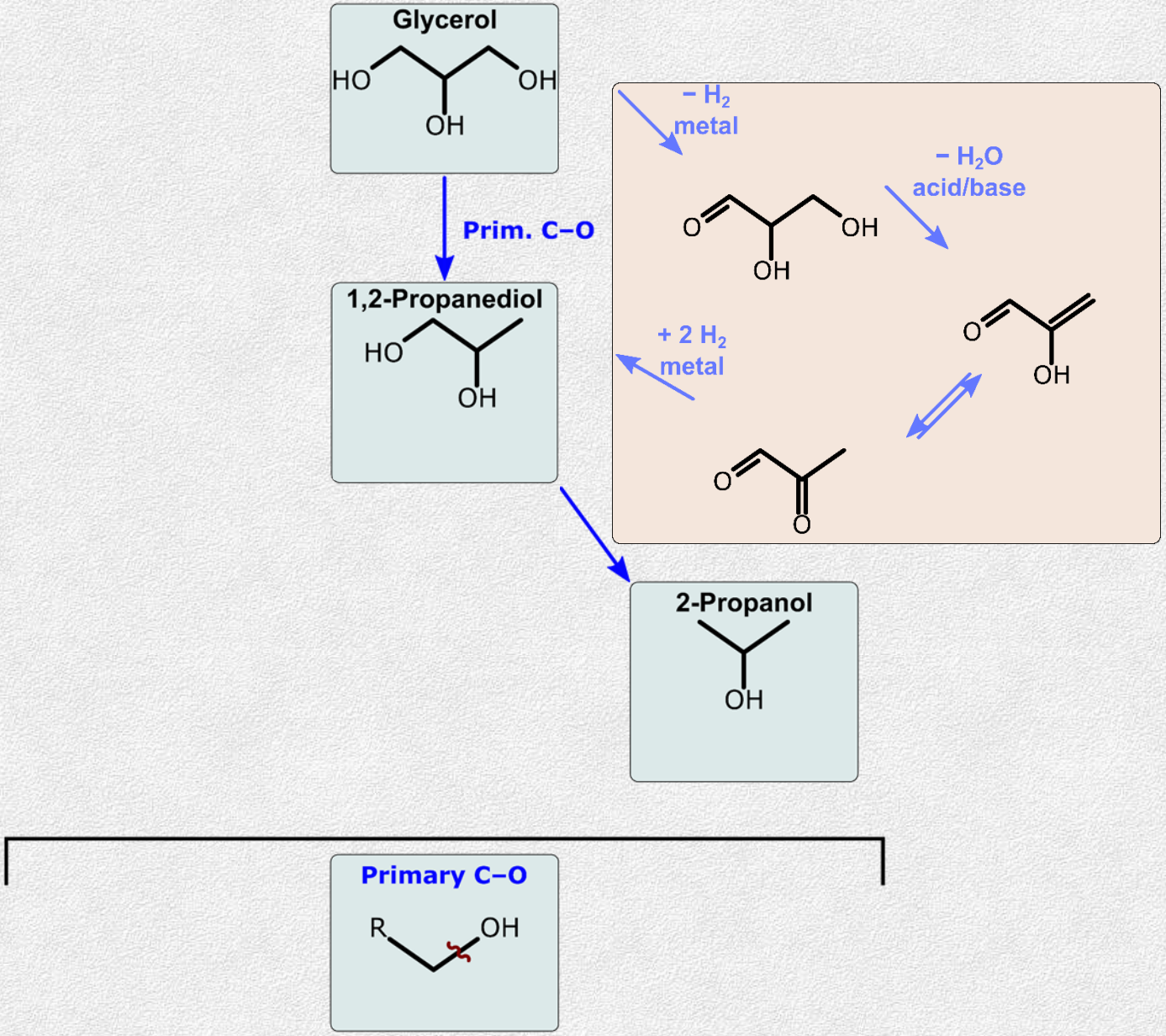
K. Tomishige, et al. ACS Catal, 2016, 6, 10, 6393

Hydrogenolysis…glycerol on Pt

Glycerol on Pt



1,2-Propanediol
2-Propanol



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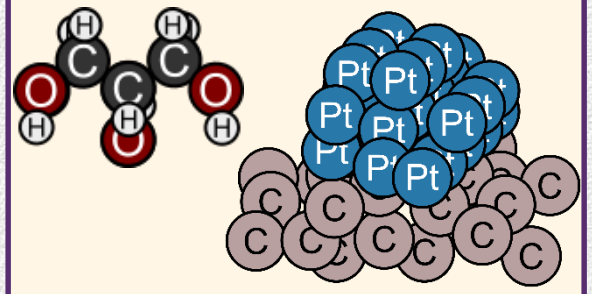
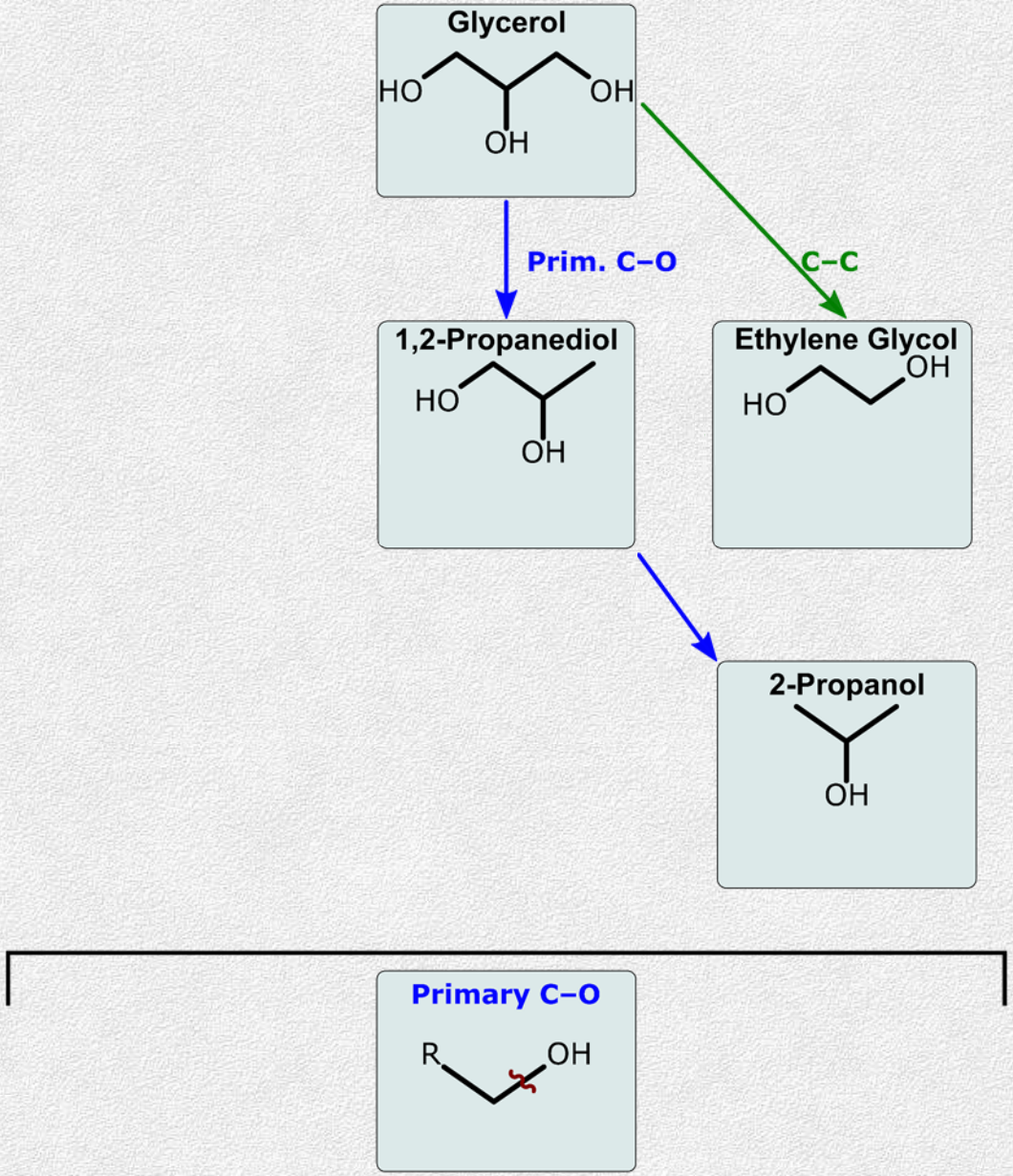


1,2-Propanediol
2-Propanol

Ethylene glycol



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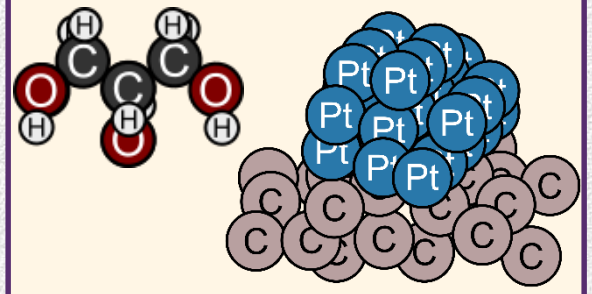
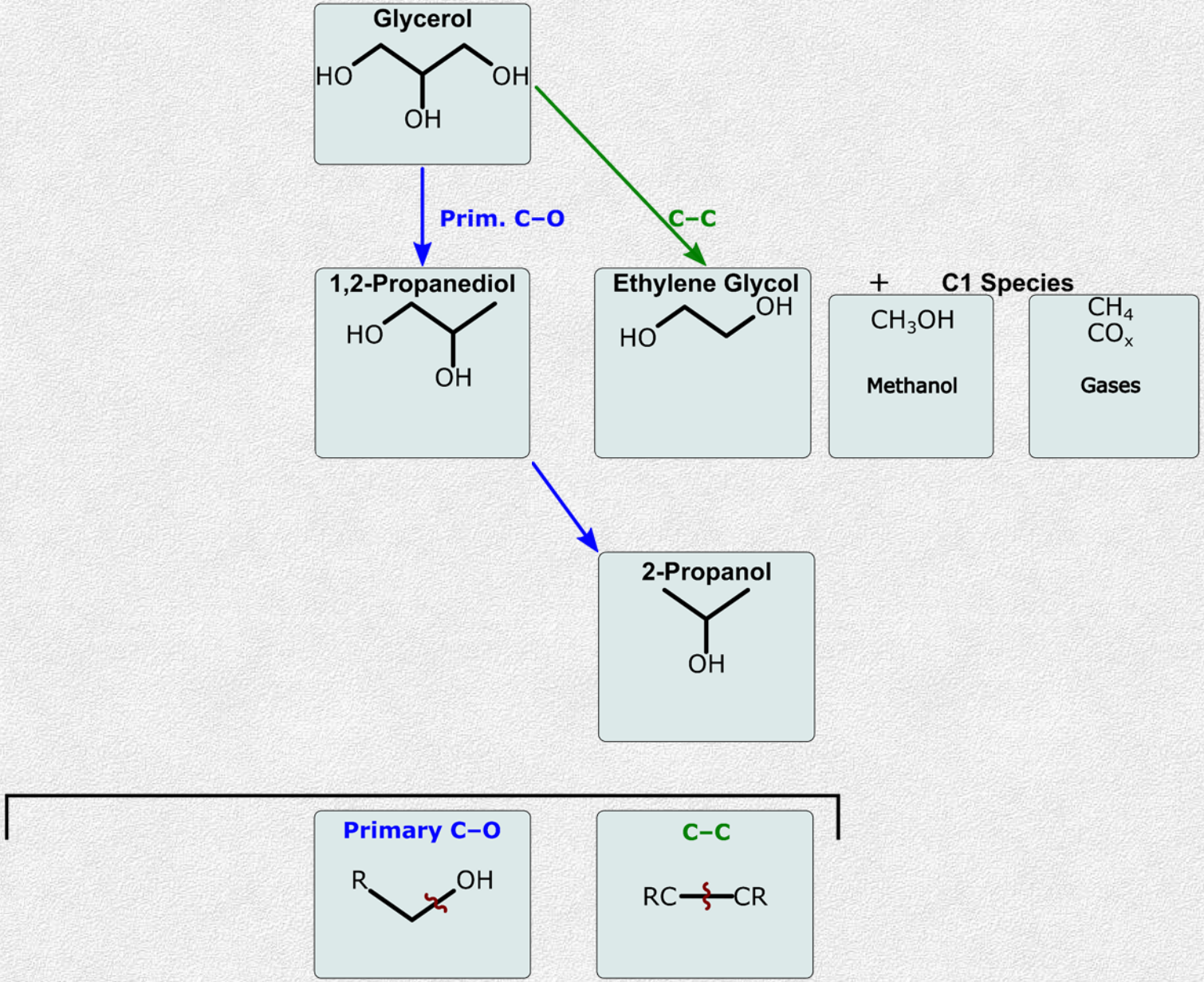


1,2-Propanediol
2-Propanol

Ethylene glycol
Methanol
Gases



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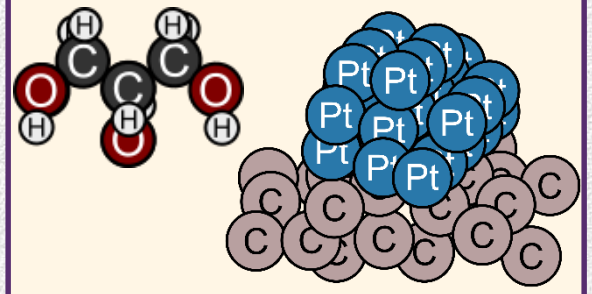
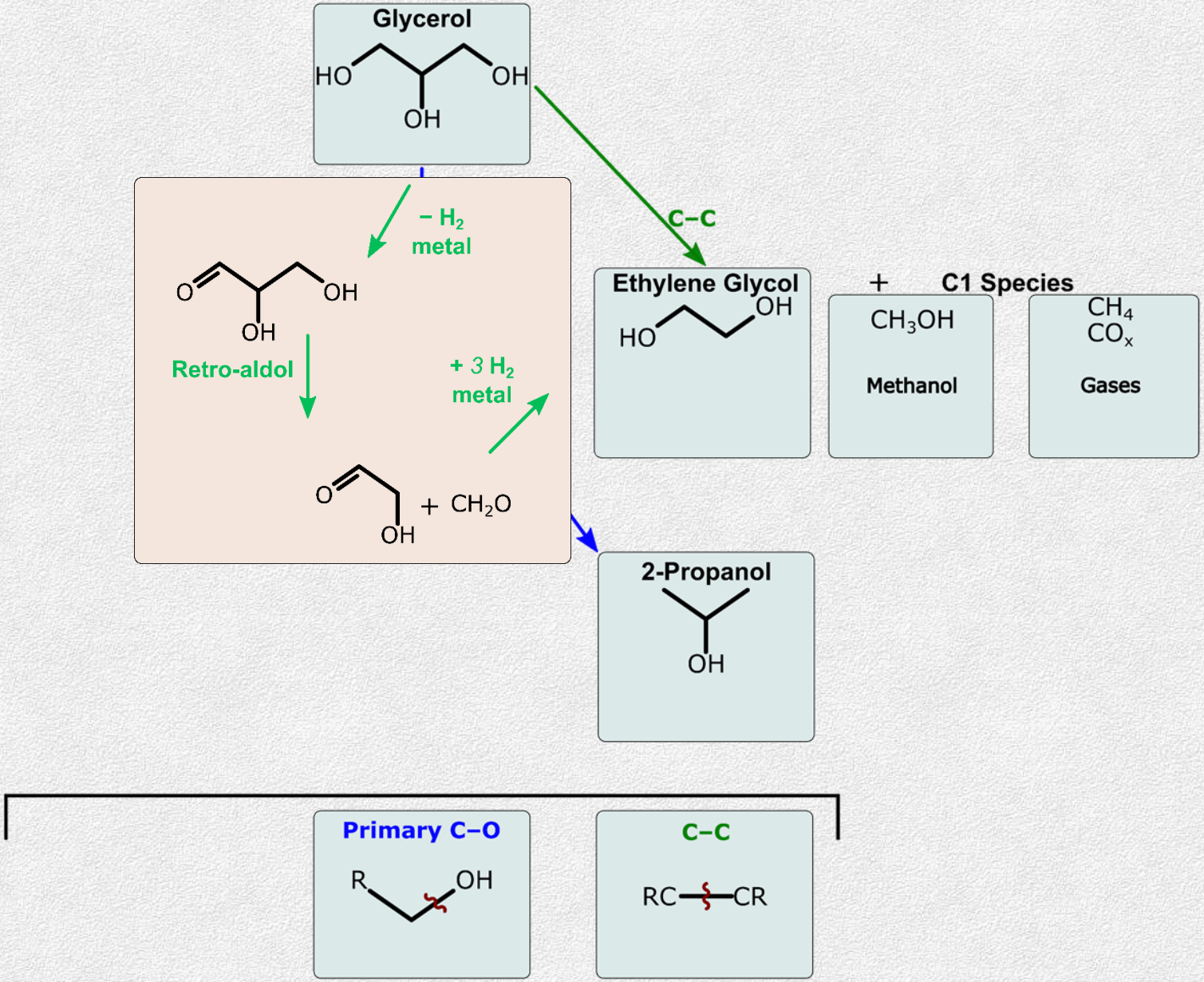


1,2-Propanediol
2-Propanol

Ethylene glycol
Methanol
Gases



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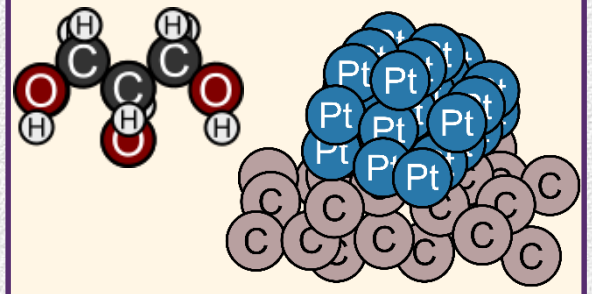
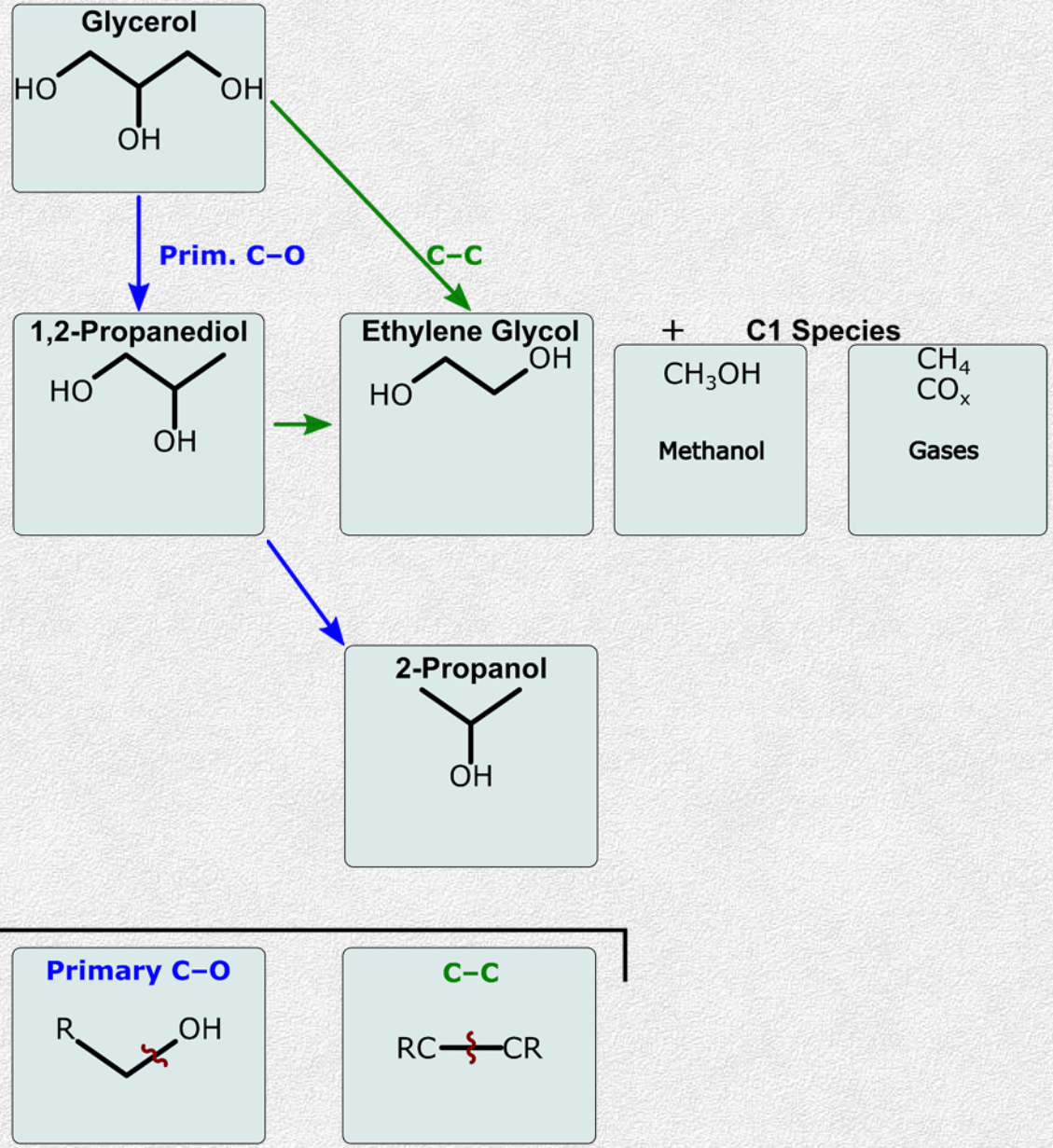


1,2-Propanediol
2-Propanol

Ethylene glycol
Methanol
Gases

Glycerol alone – no reaction

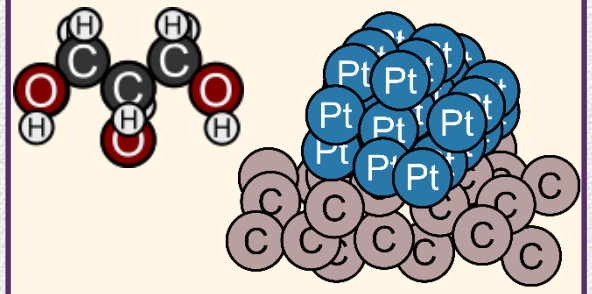
On carbon support – no reaction
(>99% carbon balance)



200 g of 1 wt. % gly/water, 200° C,
4 MPa, 0.3 g cat. (5 wt.% Pt/C), 30 hr

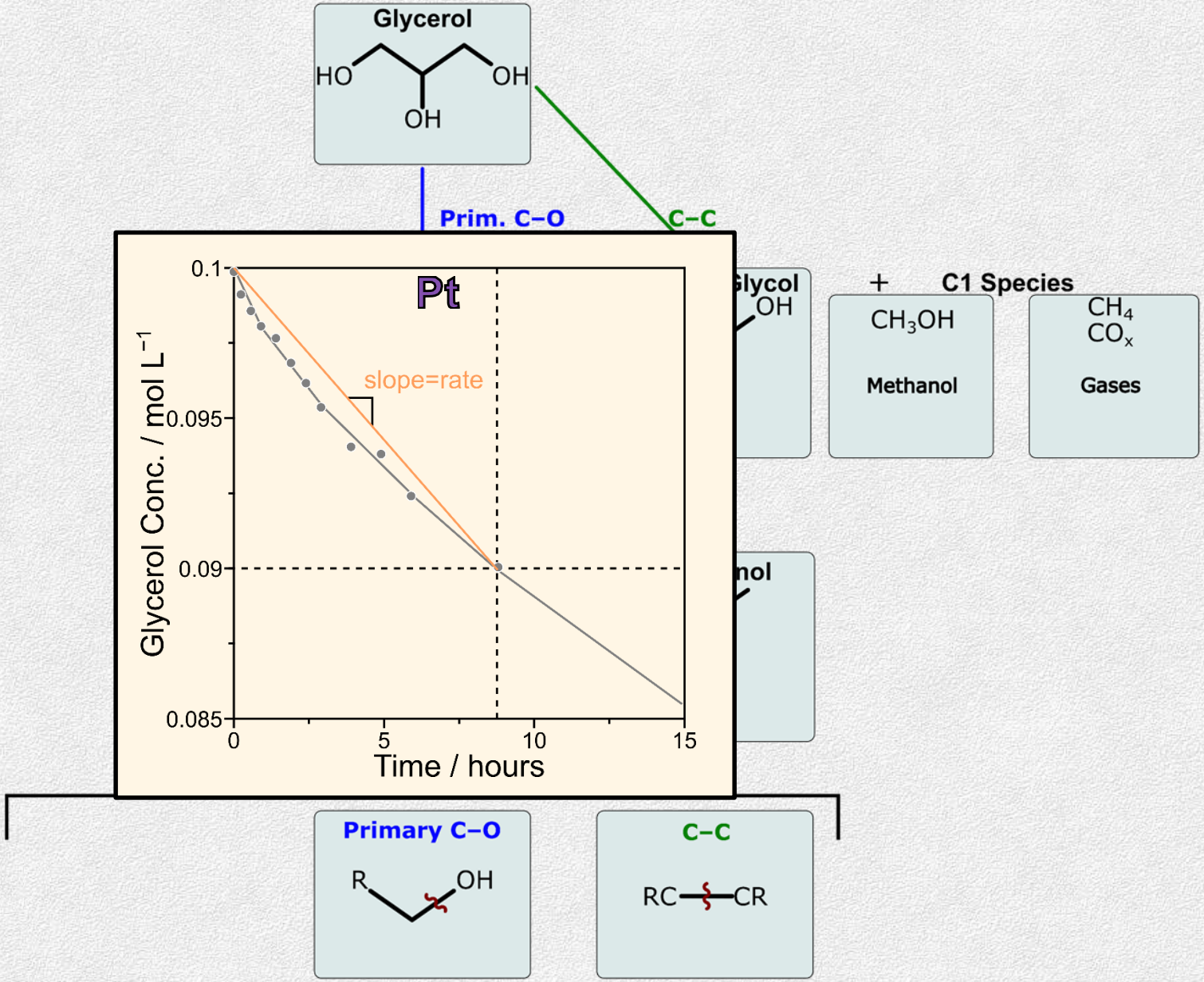
Hydrogenolysis…glycerol on Pt

Glycerol on Pt



1,2-Propanediol
2-Propanol

Ethylene glycol
Methanol
Gases



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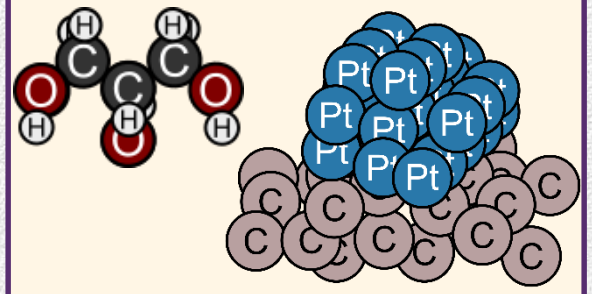
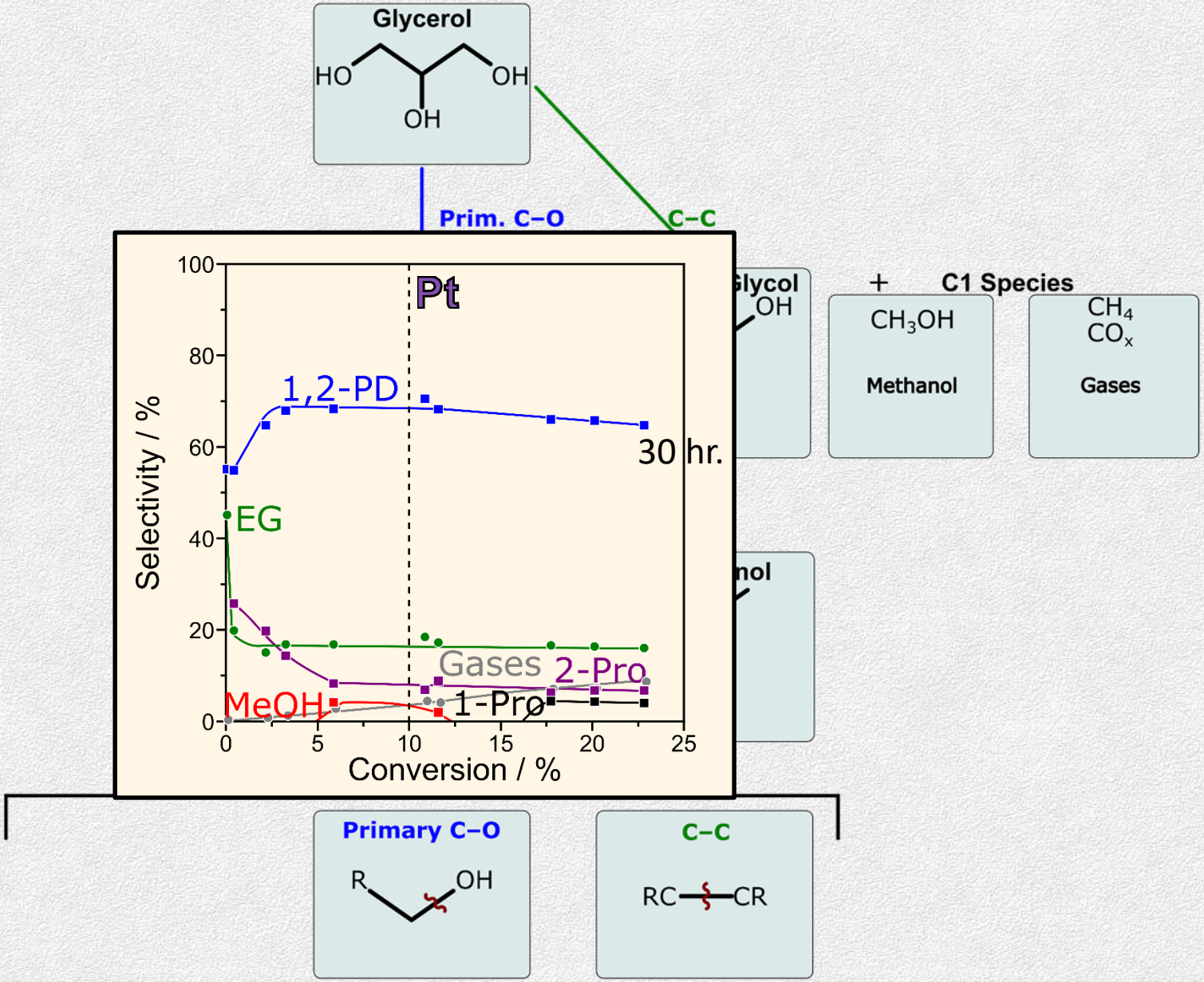


1,2-Propanediol
2-Propanol

Ethylene glycol
Methanol
Gases



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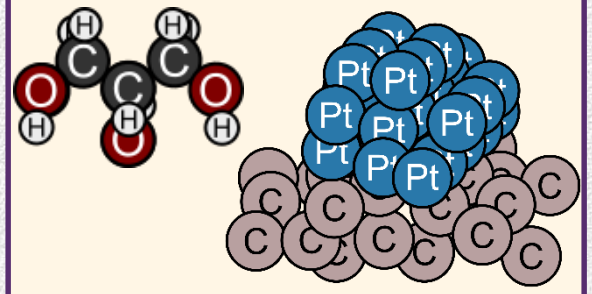
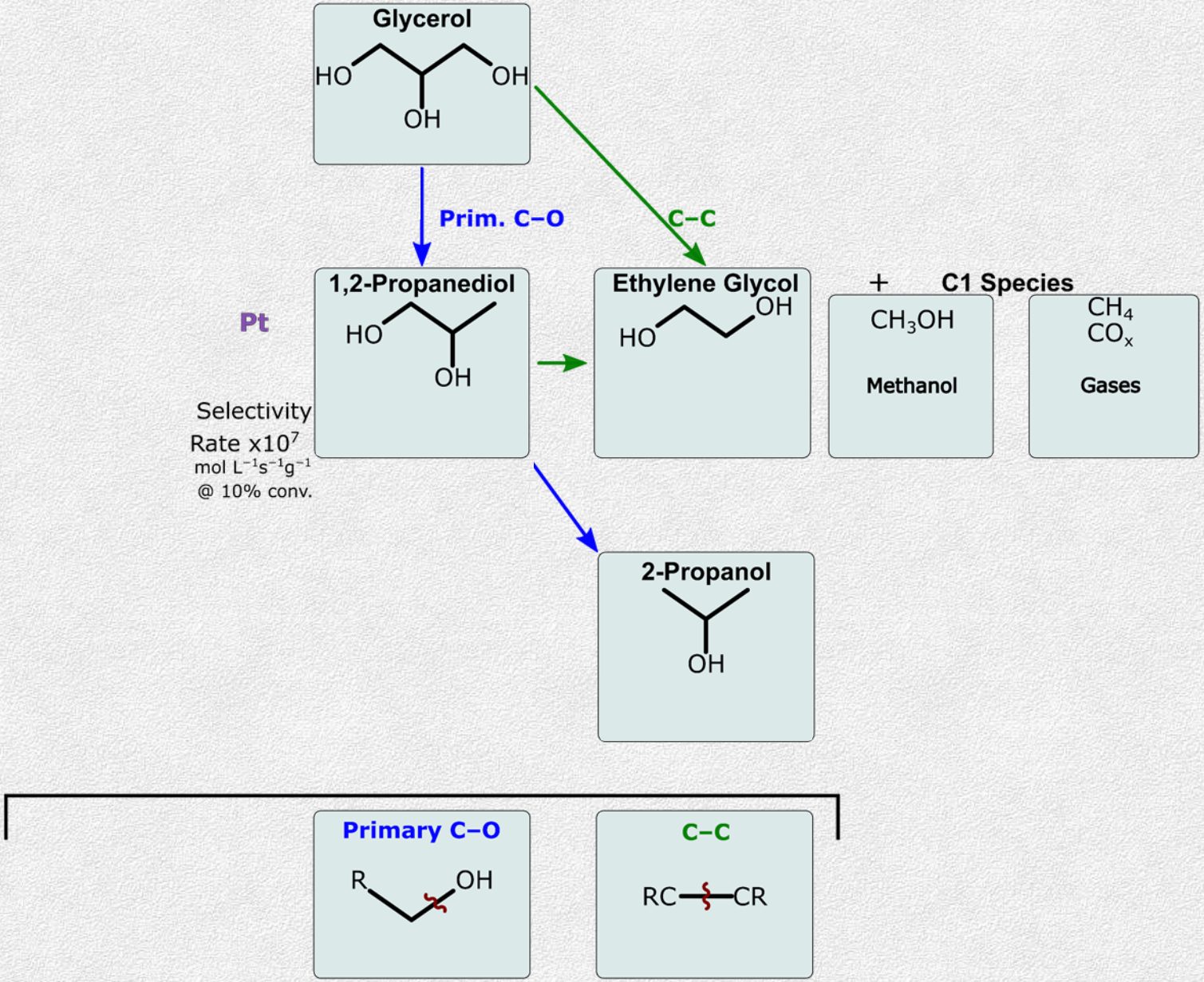


1,2-Propanediol
2-Propanol

Ethylene glycol
Methanol
Gases



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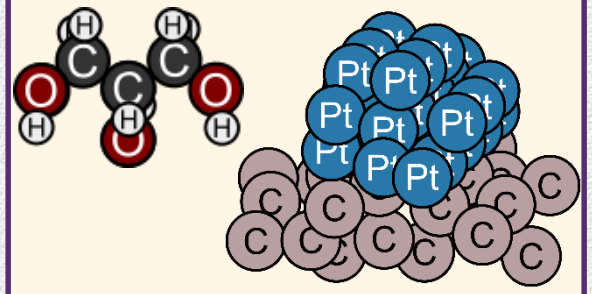
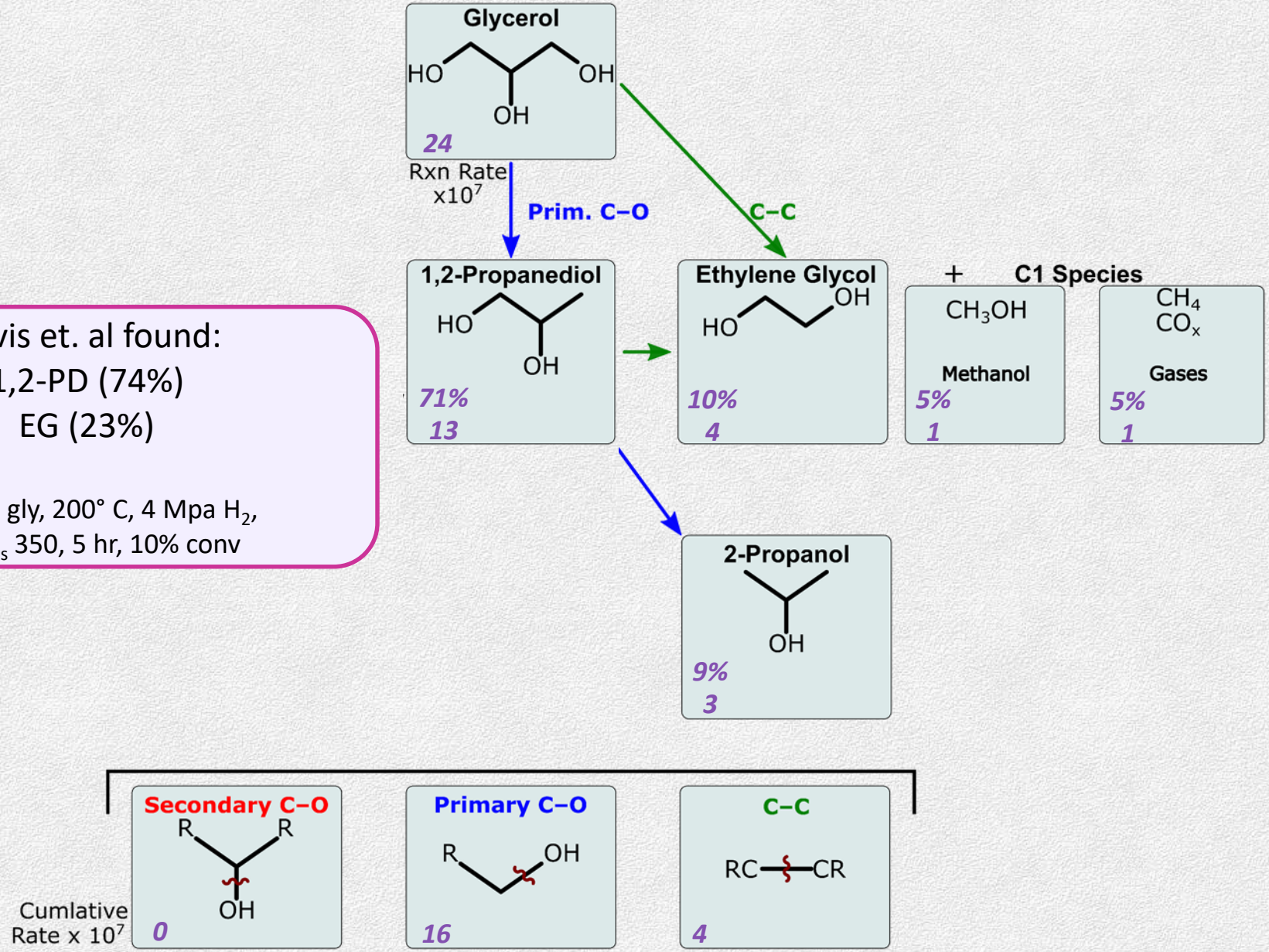


1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

Primary C–O cleavage
Some C–C cleavage

Davis et. al found:
1,2-PD (74%)
EG (23%)

1 wt. % gly, 200° C, 4 Mpa H_2,
S/M_{ads} 350, 5 hr, 10% conv



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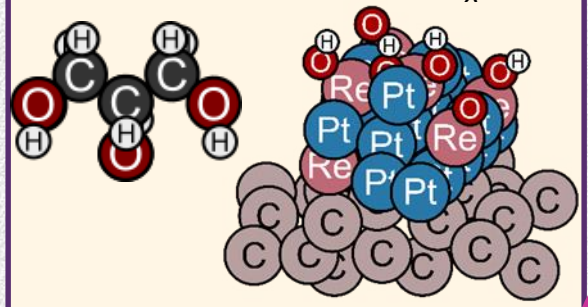
R. Davis, et al. ChemCatChem, 2010, 2, 9, 1107

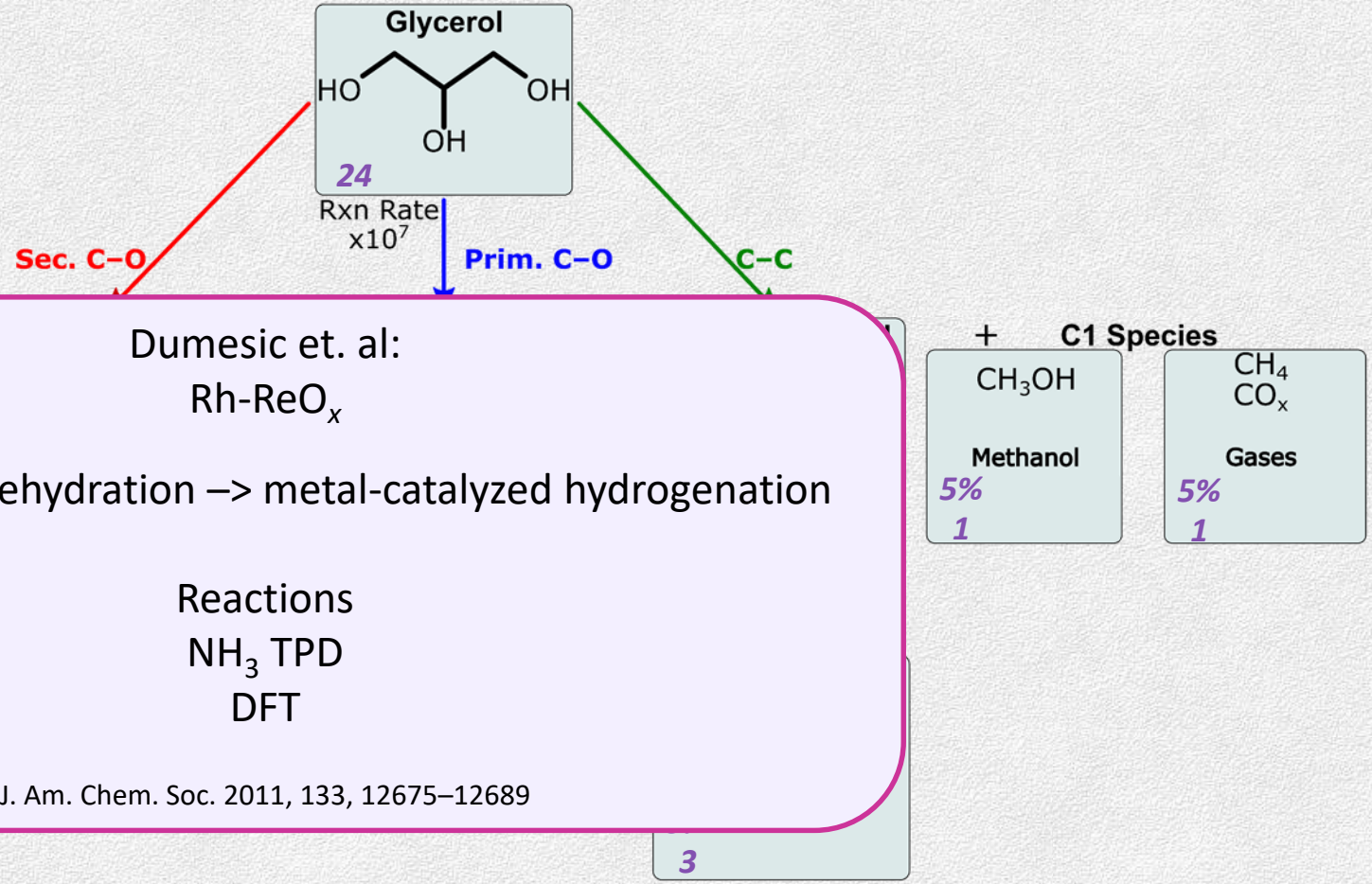
Hydrogenolysis…glycerol on $PtReO_x$

Glycerol on $PtReO_x$



1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases

Proposed ReO_x acts as a Brønsted acid



Dumesic et. al:
$Rh\text{-}ReO_x$

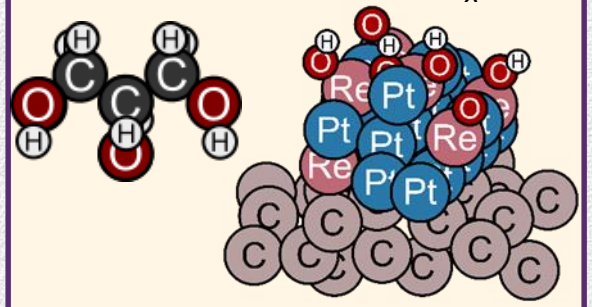
Acid-catalyzed dehydration –> metal-catalyzed hydrogenation

Reactions
NH_3 TPD
DFT

J. Am. Chem. Soc. 2011, 133, 12675–12689

Hydrogenolysis…glycerol on $PtReO_x$

Glycerol on $PtReO_x$



1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases

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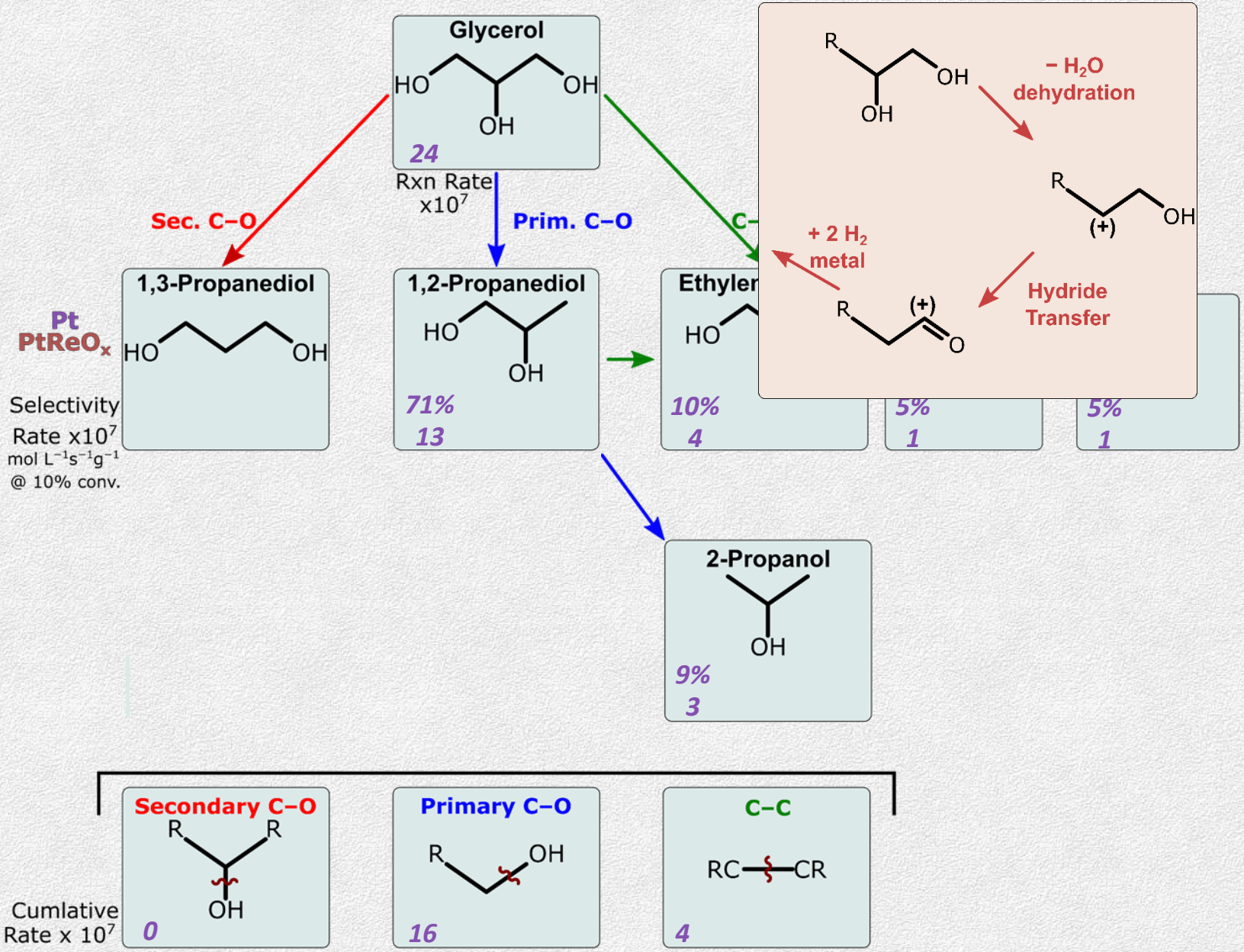

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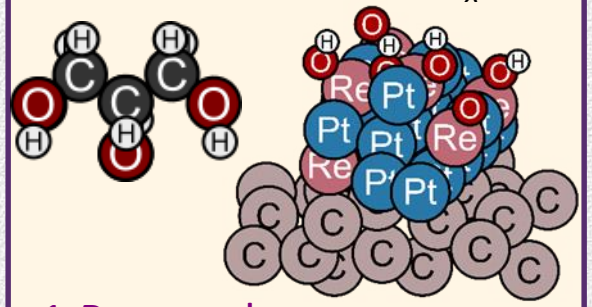

1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases

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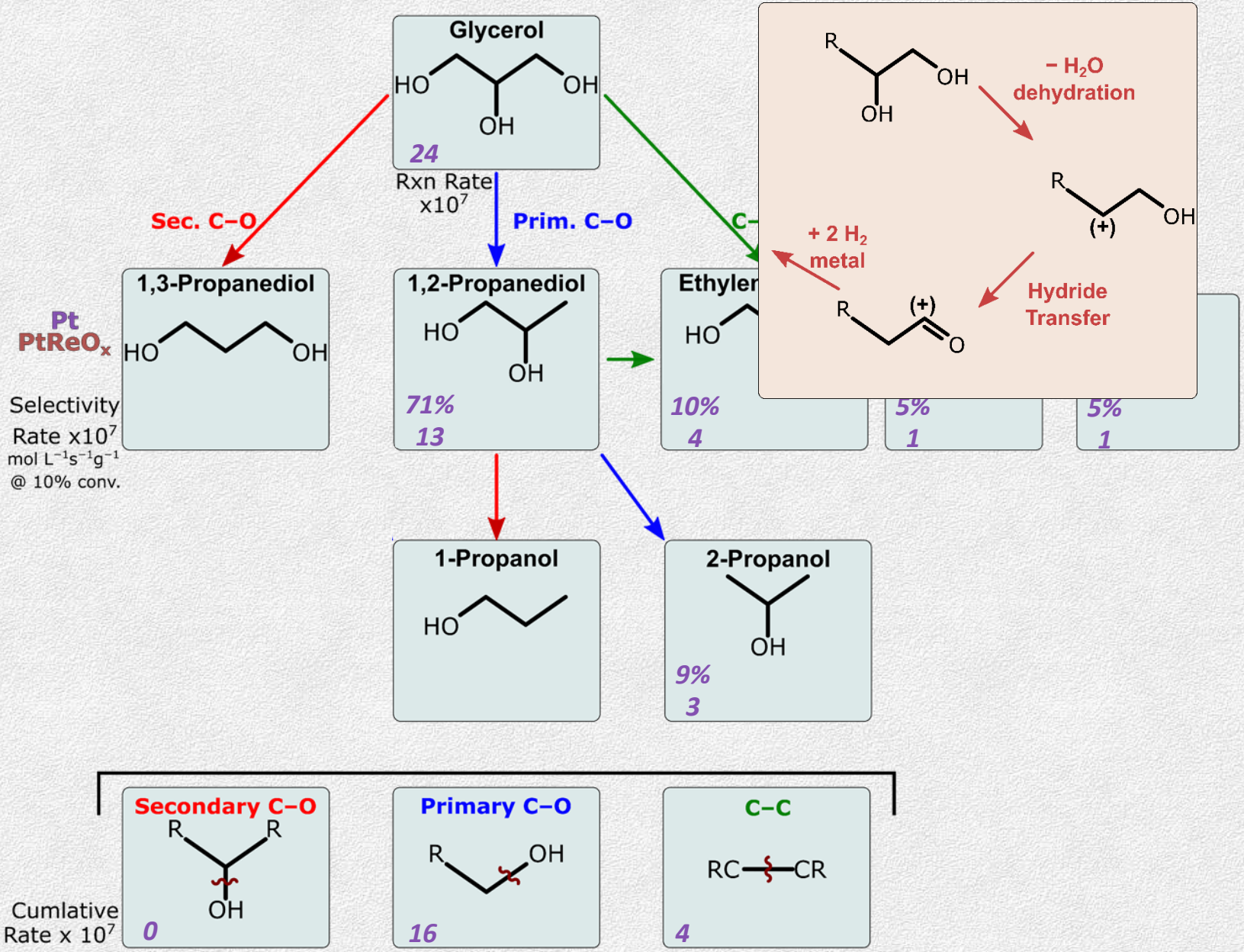

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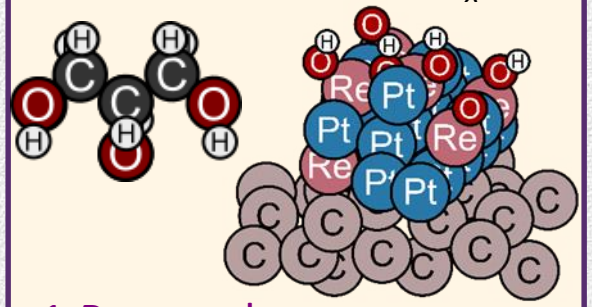
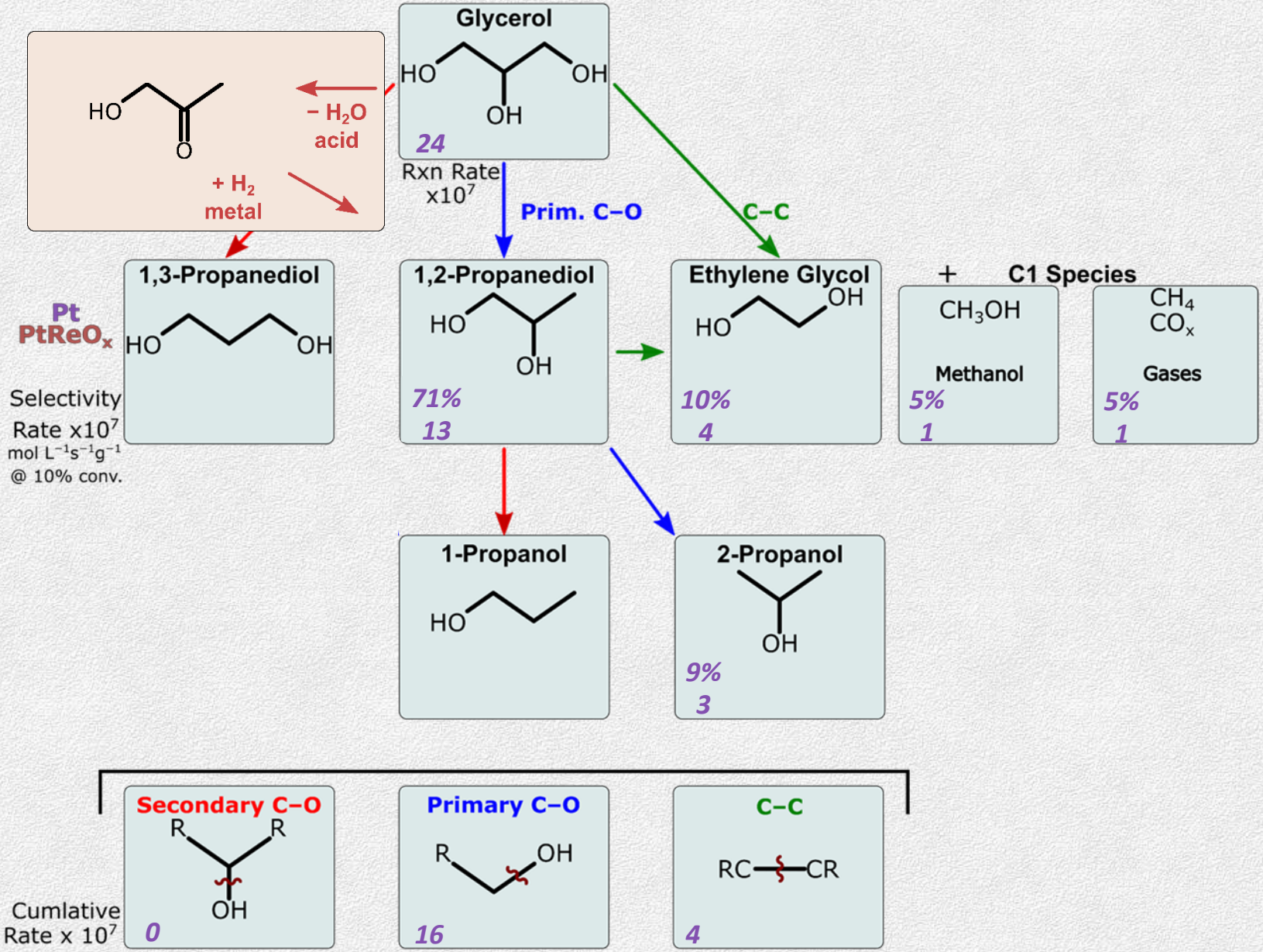


1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases

Proposed ReO_x acts as a Brønsted acid

2 paths 1,2-propanediol



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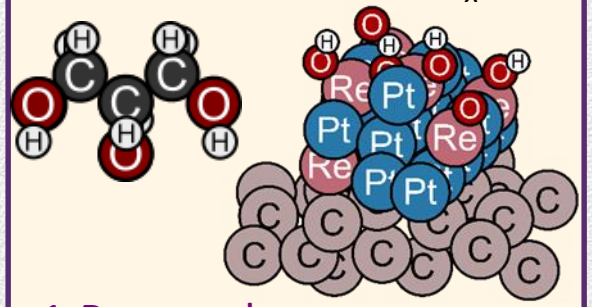
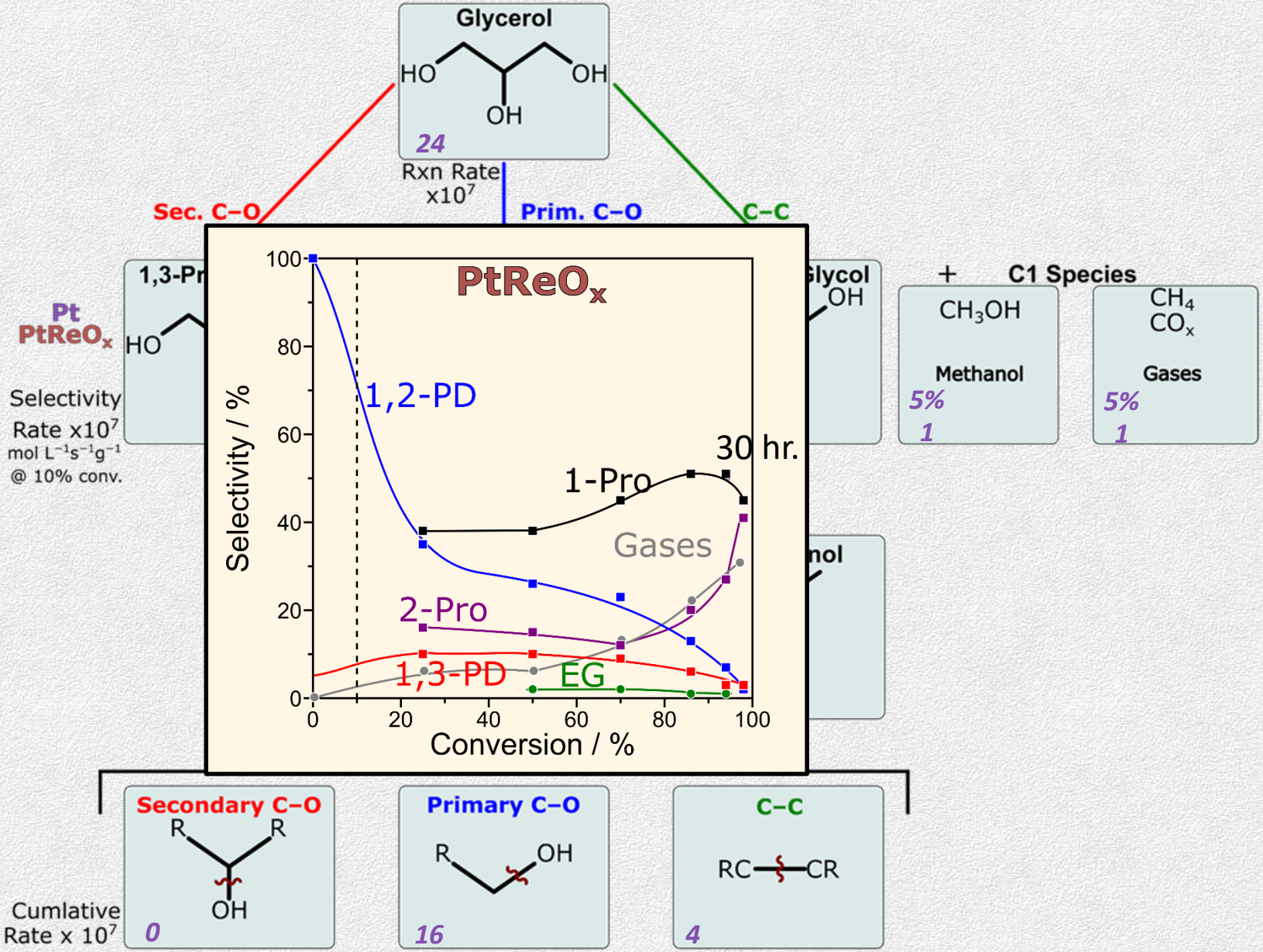


1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases



200 g of 1 wt. % gly/water, 200° C, 4 MPa, 1 g cat.(5 wt.% Pt&Re),30hr

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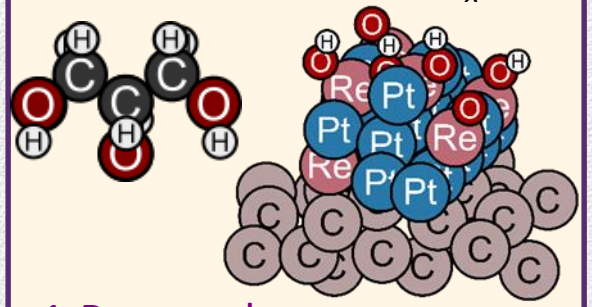
Glycerol on $PtReO_x$



1-Propanol
1,2-Propanediol
2-Propanol
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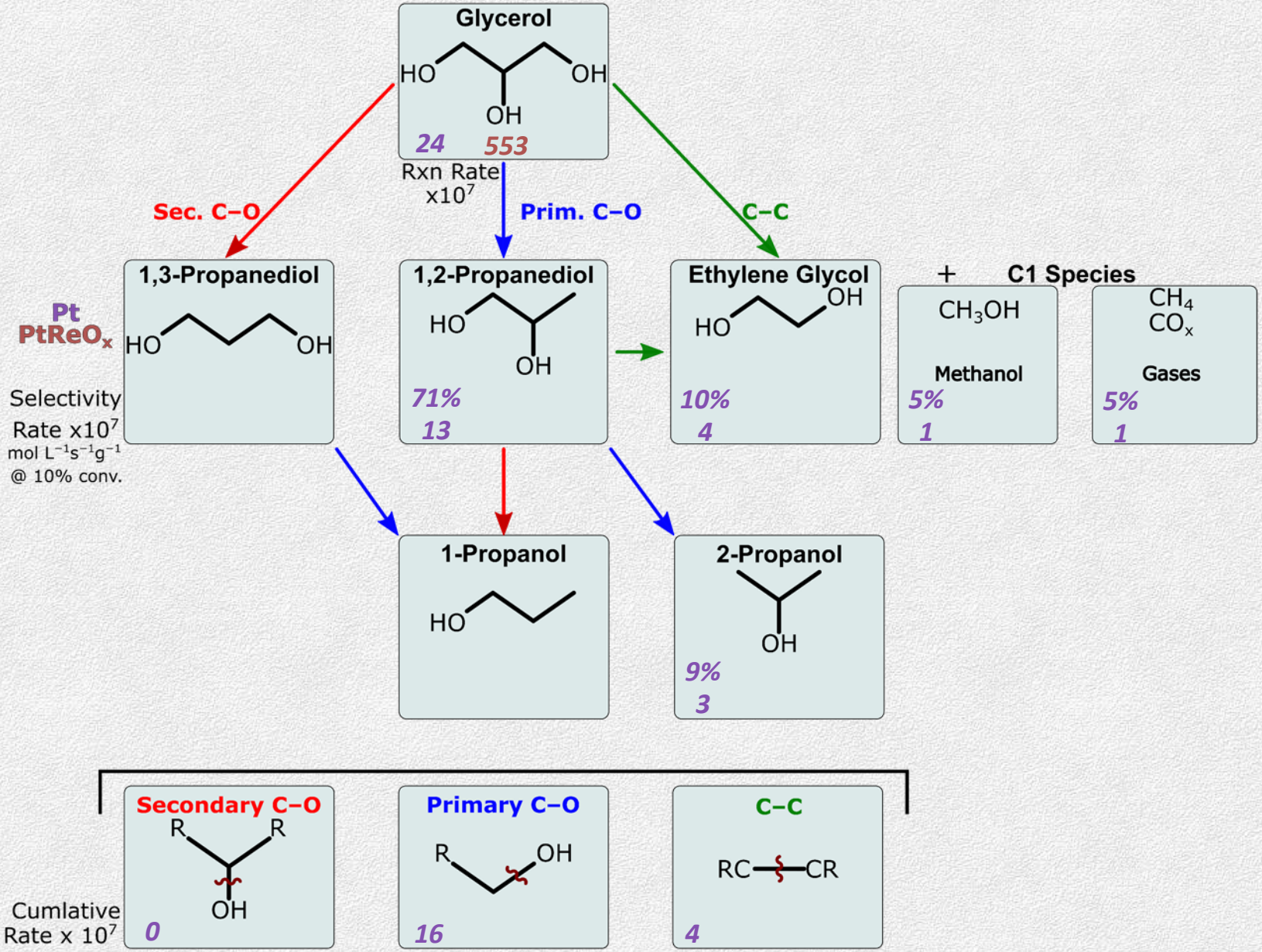
Ethylene glycol
Methanol
Gases



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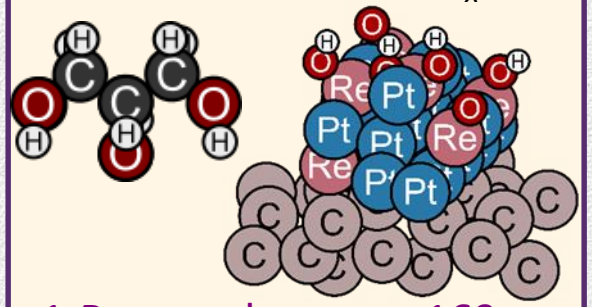
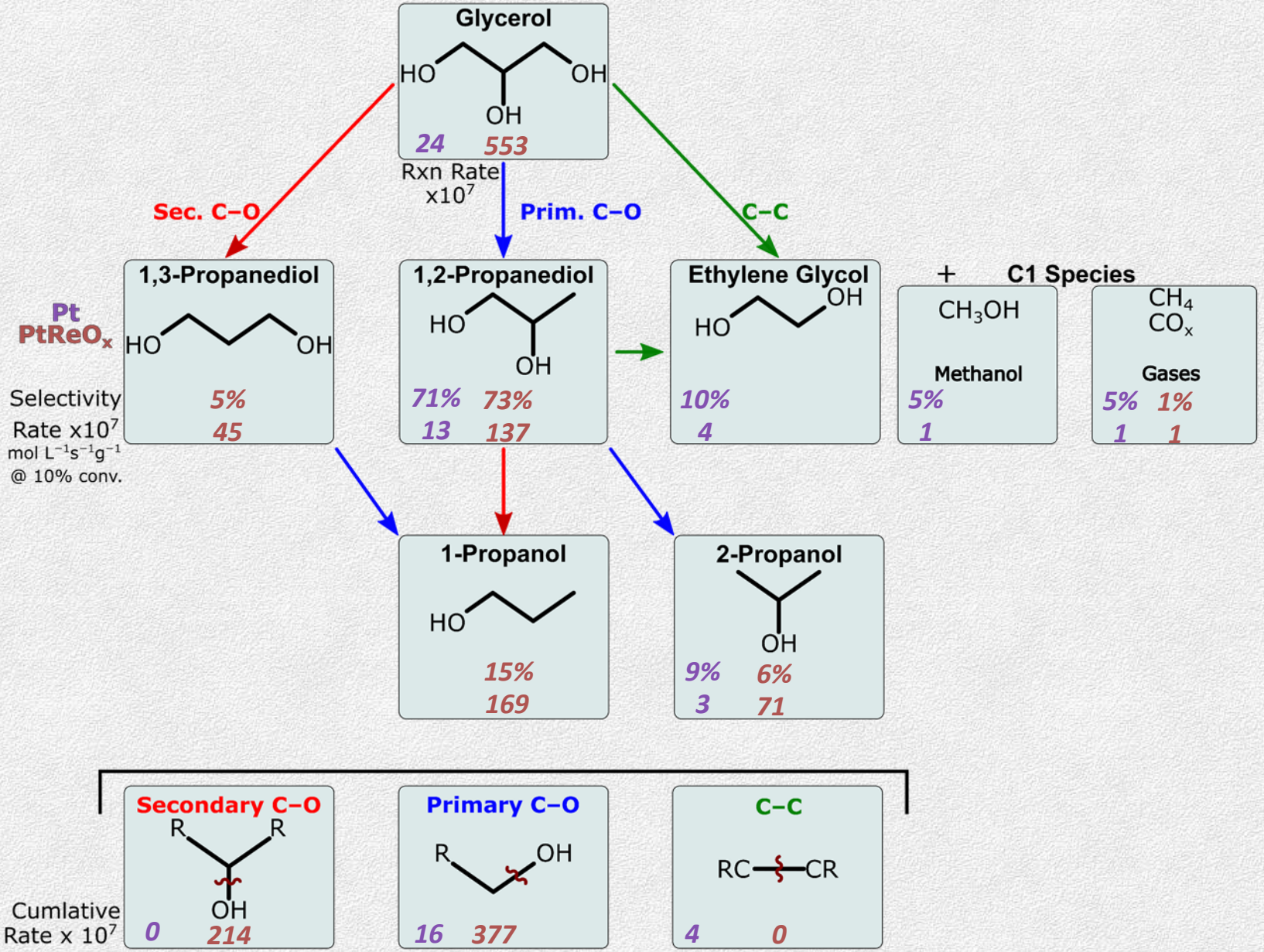


1-Propanol	169
1,2-Propanediol	137
2-Propanol	71
1,3-Propanediol	45
Ethylene glycol	0
Methanol	0
Gases	1

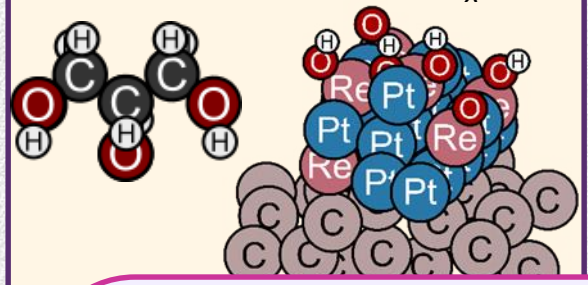
Reaction rate increased
Primary C–O increased
Negligible C–C
Facilitates secondary C–O



200 g of 1 wt. % gly/water, 200° C,
4 MPa, 1 g cat.(5 wt.% Pt&Re),30hr

Hydrogenolysis…glycerol on $PtReO_x$

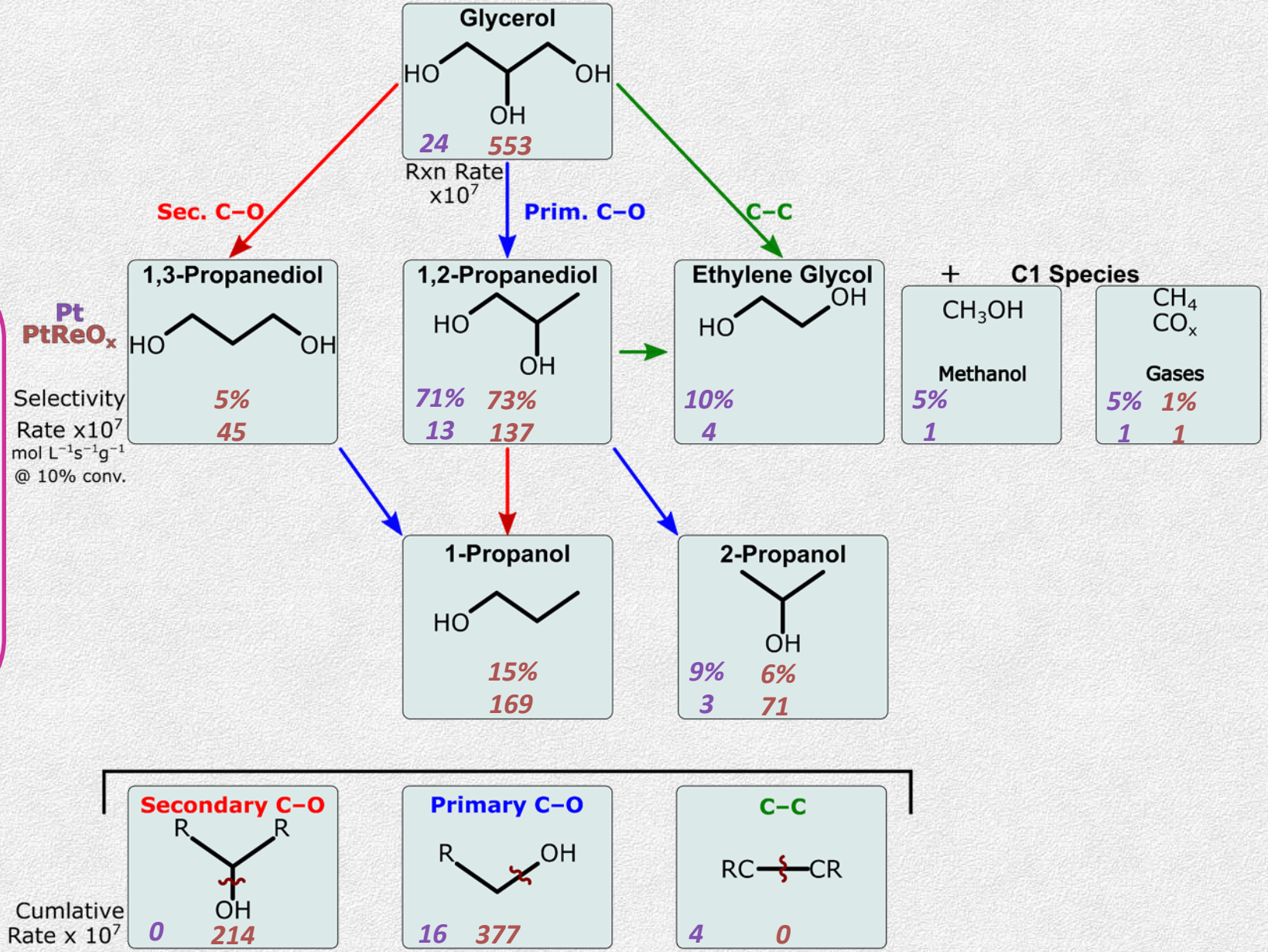
Glycerol on $PtReO_x$



Davis et. al found:
1,2-Propanediol (36%)
1-Propanol (25%)
1,3-Propanediol (15%)
Ethanol (9%)
2-Propanol (8%)
EG (8%)

1 wt. % gly, 200° C, 4 Mpa H_2, S/M_{ads} 350, 5 hr, 50% conv

Pt
Negligible C–C
Facilitates secondary C–O

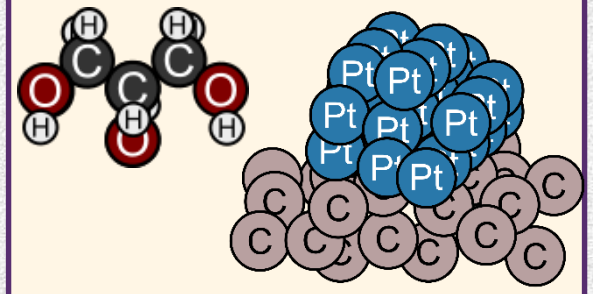


200 g of 1 wt. % gly/water, 200° C, 4 MPa, 1 g cat.(5 wt.% Pt&Re),30hr

R. Davis, et al. ChemCatChem, 2010, 2, 9, 1107

Hydrogenolysis of glycerol

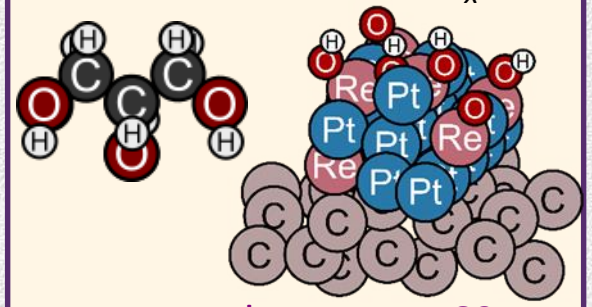
Glycerol on Pt



1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

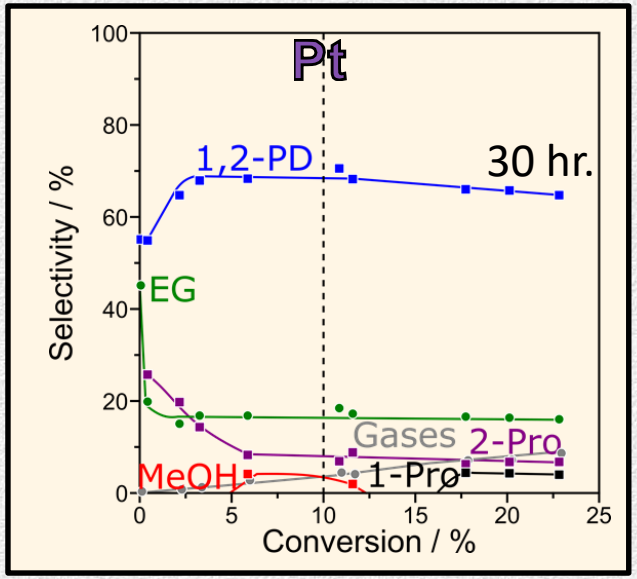
Primary C–O cleavage
Some C–C cleavage

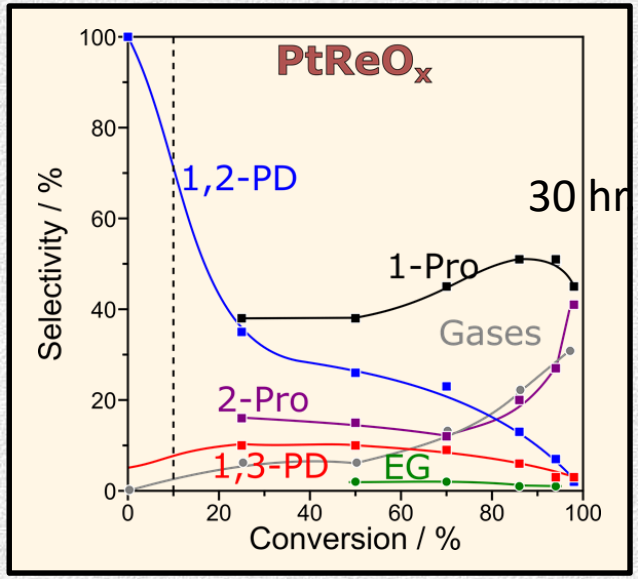
Glycerol on $PtReO_x$



1-Propanol	169
1,2-Propanediol	137
2-Propanol	71
1,3-Propanediol	25
Ethylene glycol	0
Methanol	0
Gases	1

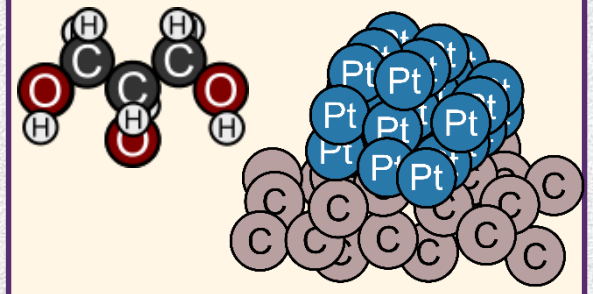
Reaction rate increased
Primary C–O increased
Negligible C–C
Facilitates secondary C–O





Hydrogenolysis of glycerol

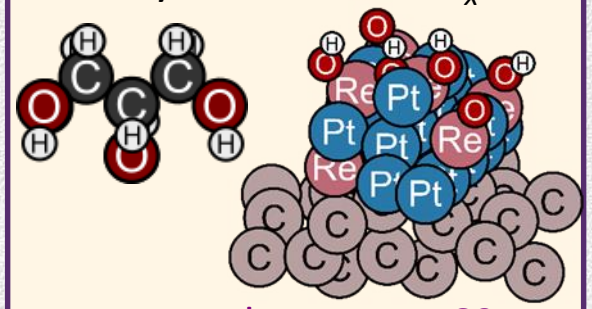
Glycerol on Pt



1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

Primary C–O cleavage
Some C–C cleavage

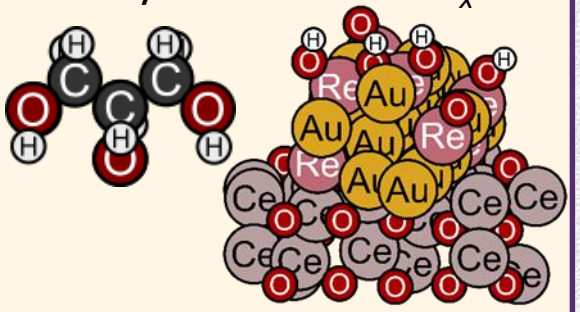
Glycerol on $PtReO_x$



1-Propanol	169
1,2-Propanediol	137
2-Propanol	71
1,3-Propanediol	25
Ethylene glycol	0
Methanol	0
Gases	1

Reaction rate increased
Primary C–O increased
Negligible C–C
Facilitates secondary C–O

Glycerol on $AuReO_x$



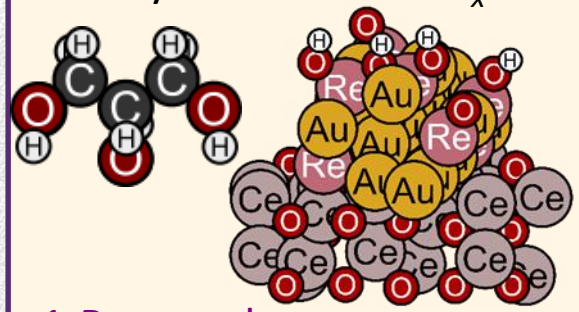
Poor hydrogenation cat.

Unsaturated Products

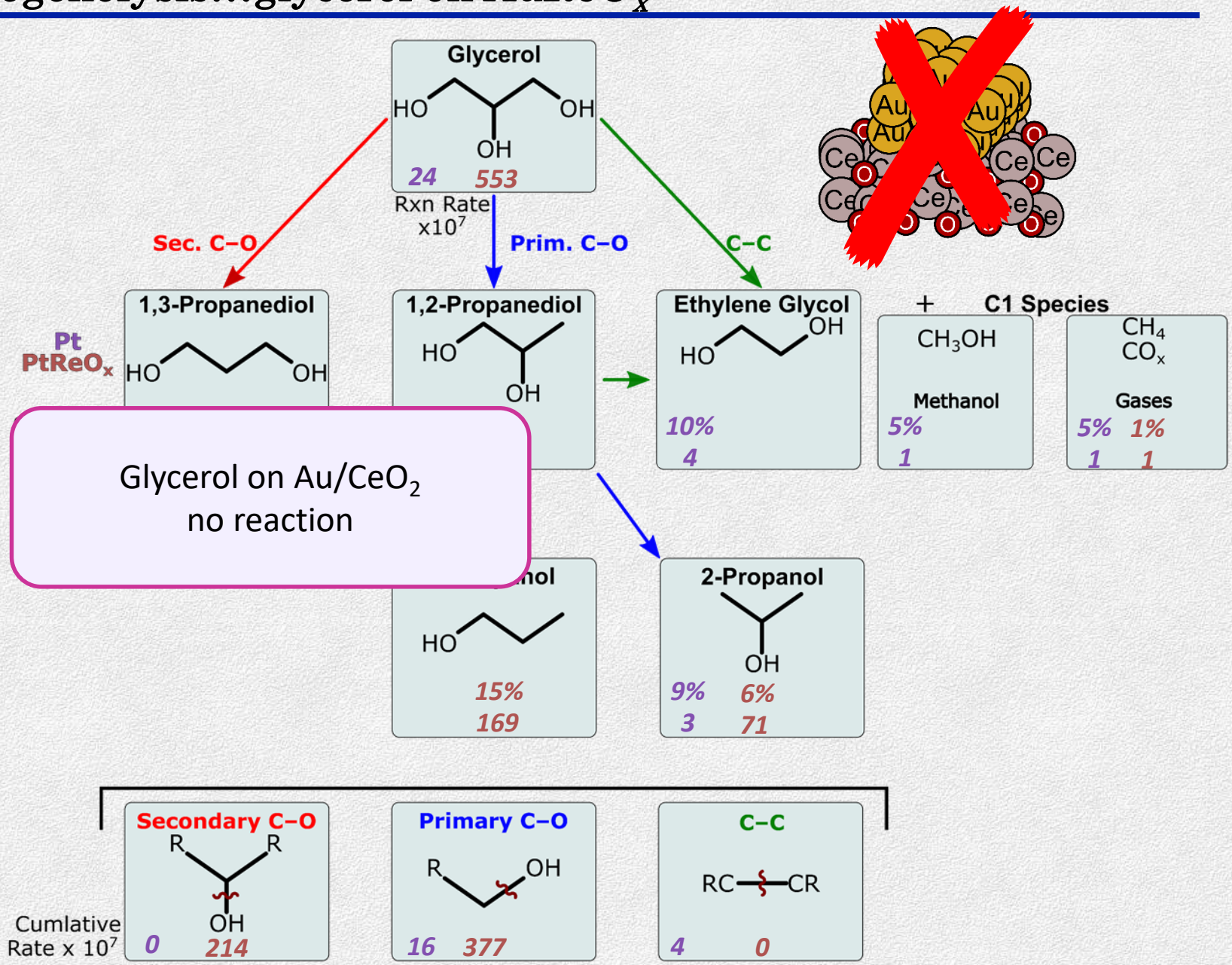
Help identify intermediates

Hydrogenolysis…glycerol on $AuReO_x$

Glycerol on $AuReO_x$

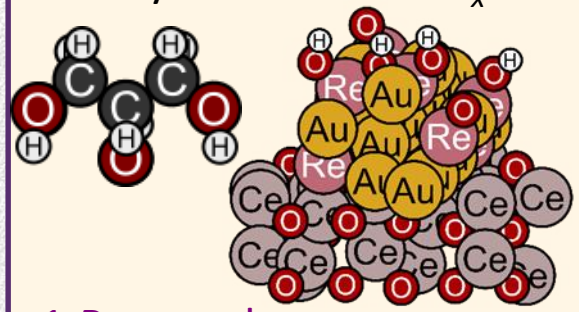


1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases

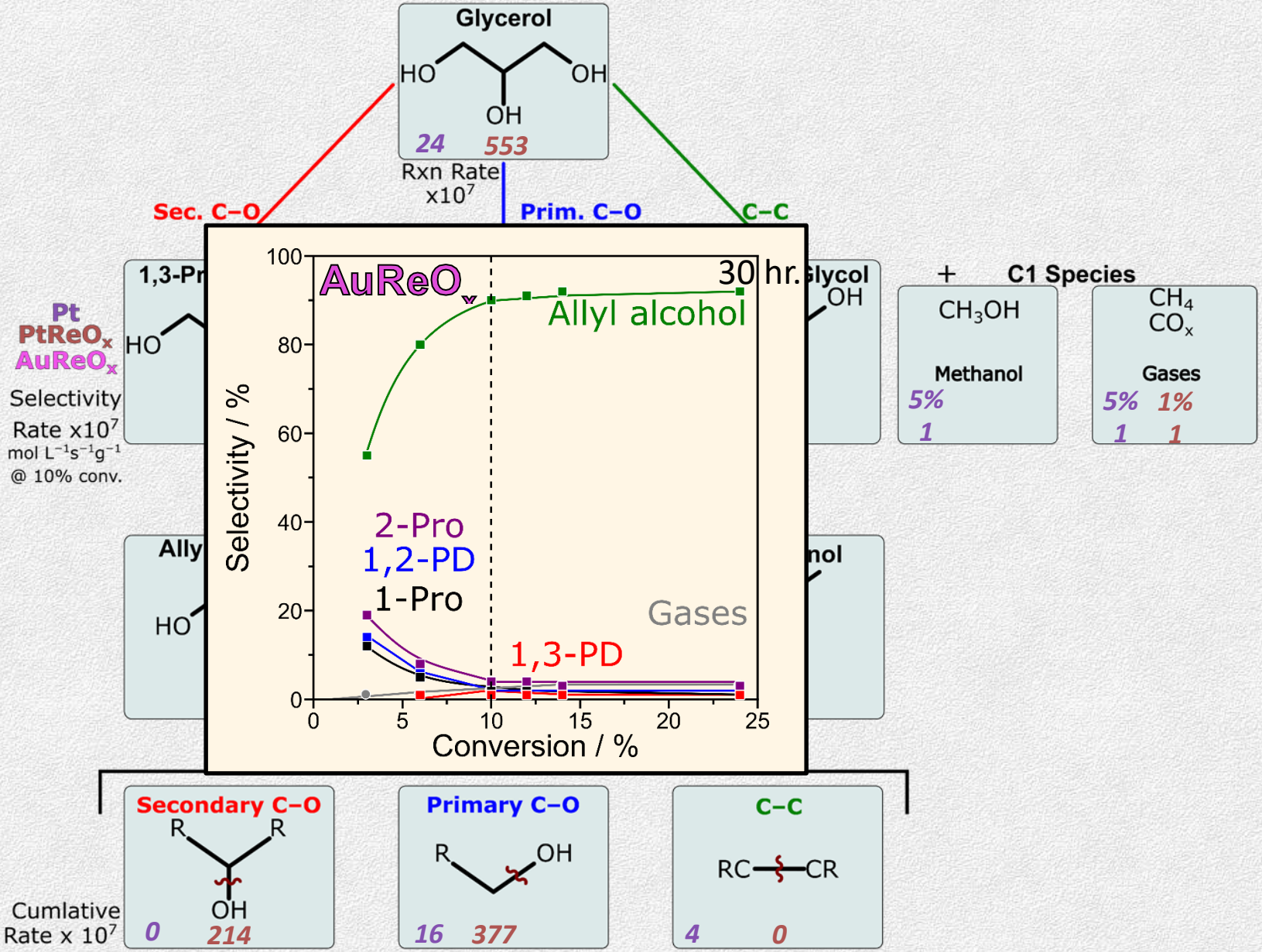


Hydrogenolysis…glycerol on $AuReO_x$

Glycerol on $AuReO_x$



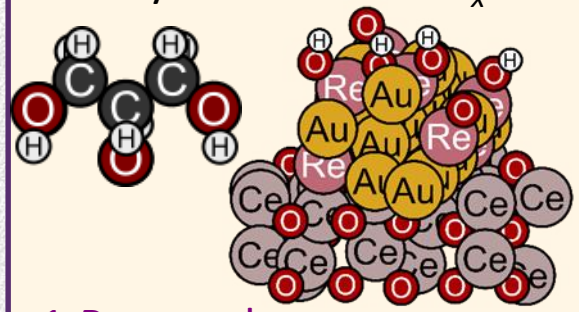
1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases
Allyl alcohol



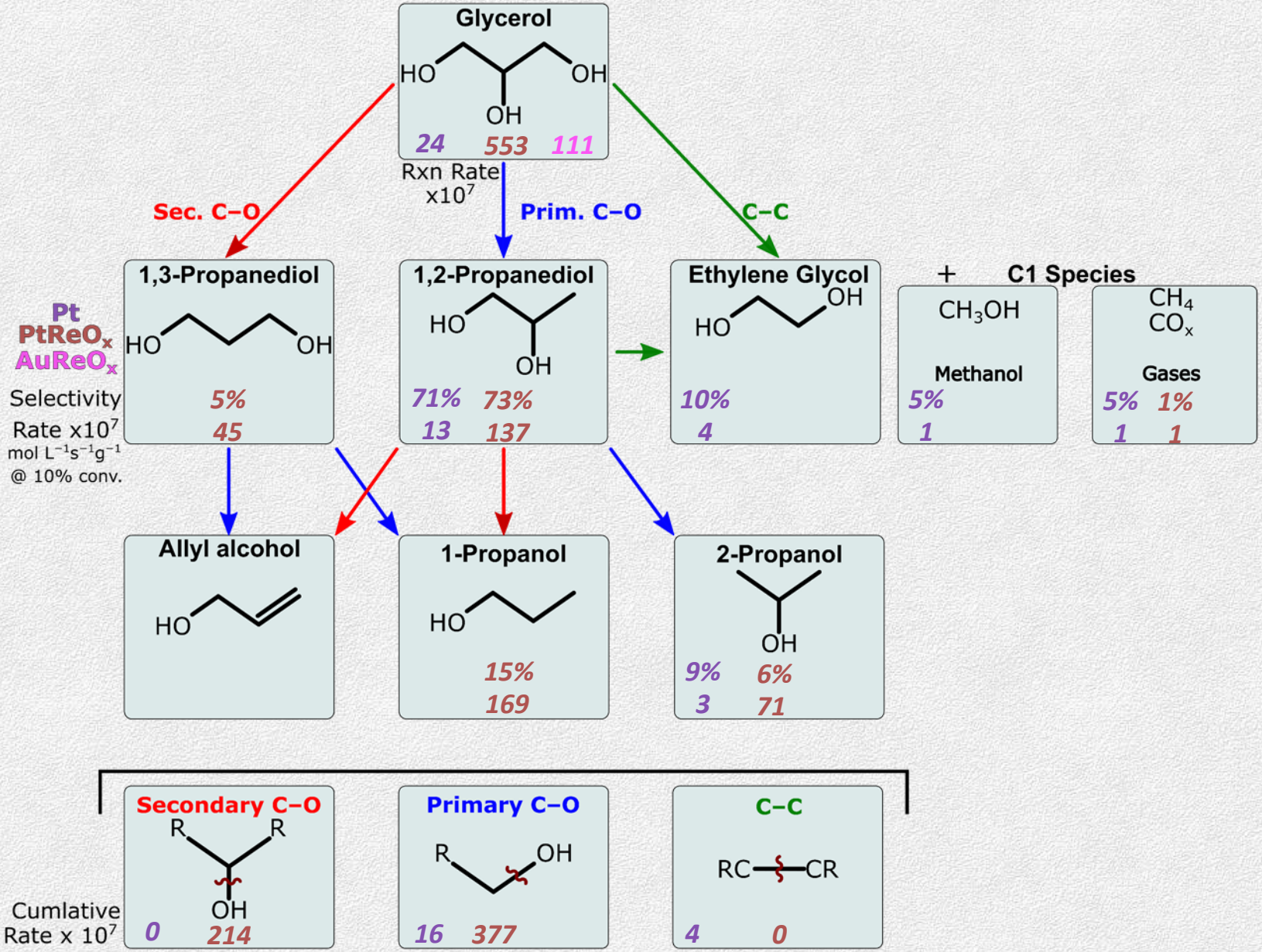
200 g of 1 wt. % gly/water, 200° C, 4MPa,0.1 g cat.(1:0.3 wt.%Au:Re),30hr

Hydrogenolysis…glycerol on $AuReO_x$

Glycerol on $AuReO_x$



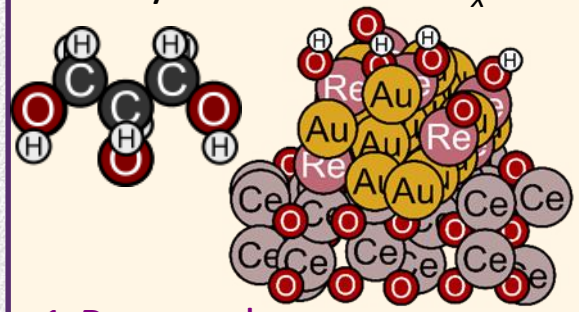
1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases
Allyl alcohol



200 g of 1 wt. % gly/water, 200° C, 4MPa,0.1 g cat.(1:0.3 wt.%Au:Re),30hr

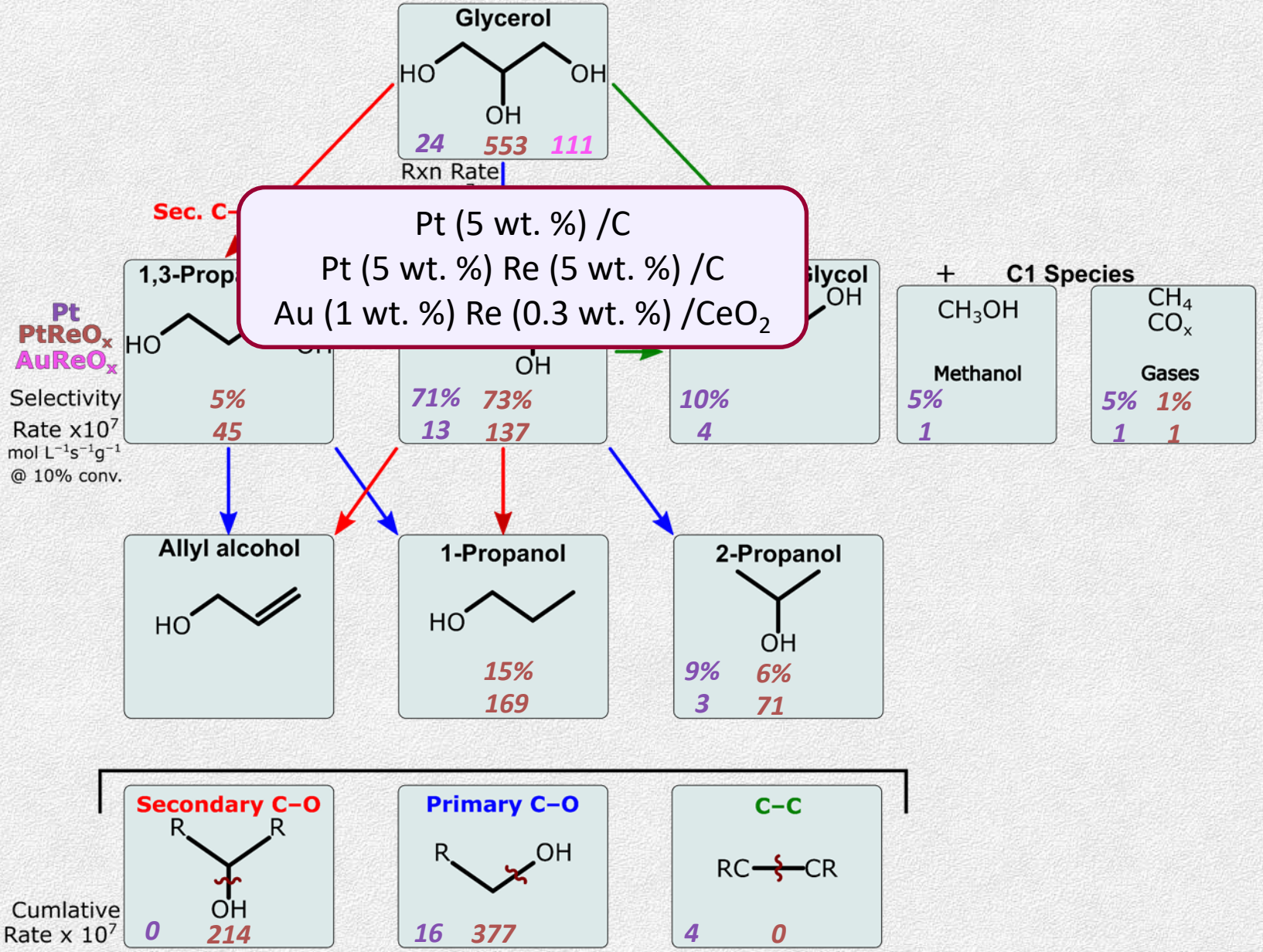
Hydrogenolysis…glycerol on $AuReO_x$

Glycerol on $AuReO_x$



1-Propanol
1,2-Propanediol
2-Propanol
1,3-Propanediol
Ethylene glycol
Methanol
Gases
Allyl alcohol

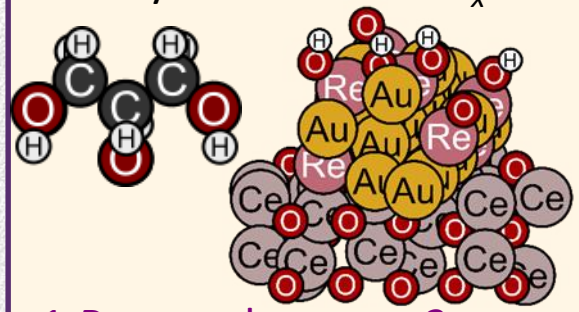
Rates $PtReO_x$>$AuReO_x$>Pt



200 g of 1 wt. % gly/water, 200° C, 4MPa,0.1 g cat.(1:0.3 wt.%Au:Re),30hr

Hydrogenolysis…glycerol on $AuReO_x$

Glycerol on $AuReO_x$



1-Propanol 2

1,2-Propanediol 2

2-Propanol 1

1,3-P

Ethy

Met

Gase

Allyl

Rates

Negligible C–C cleavage

Increased C–O cleavage

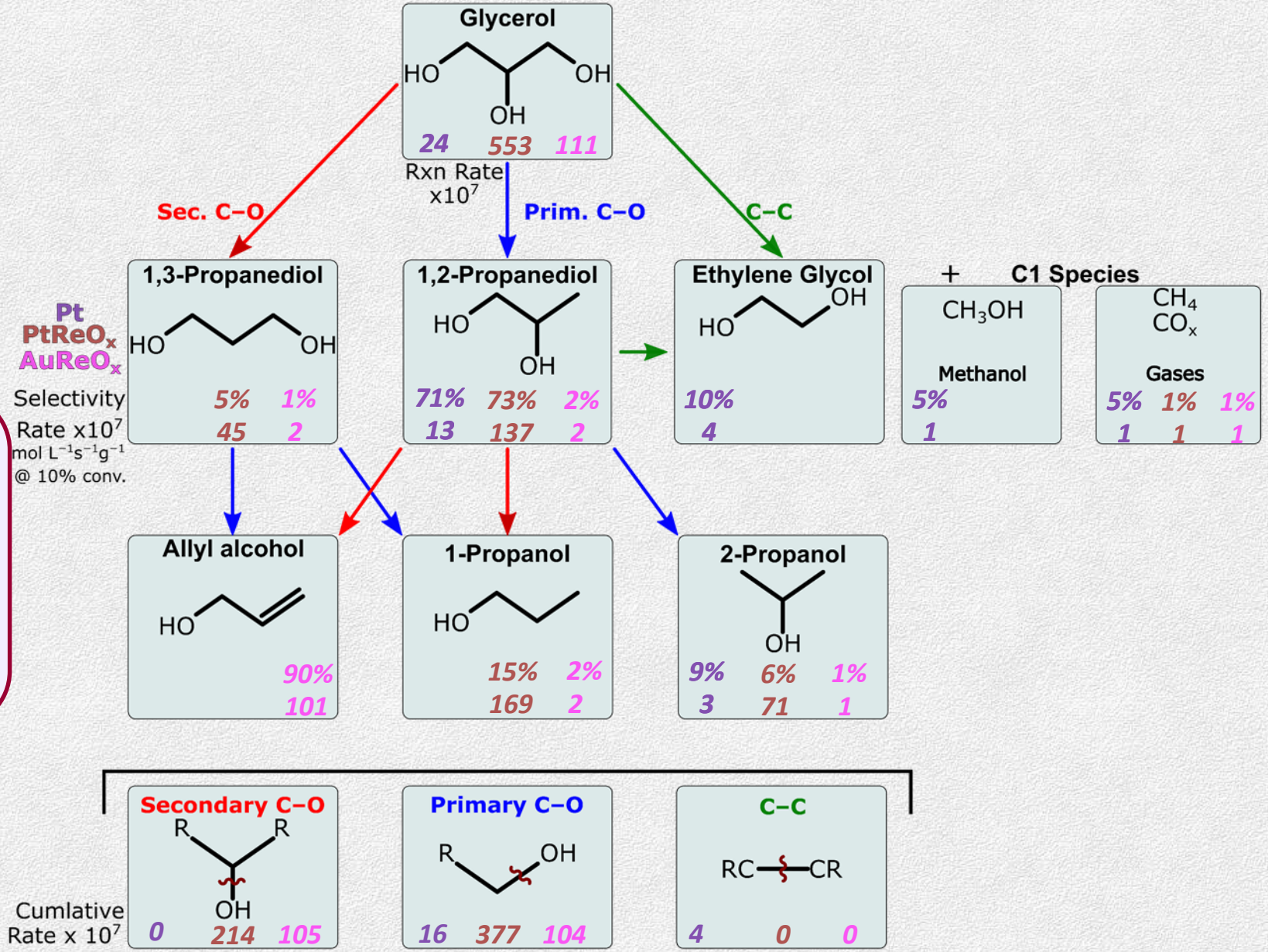
unsaturated

Tomishege:

Allyl alcohol (91%)

1-Propanol (5%)

0.3 g gly, 0.5 g AuRe, 4 g 1,4-dioxnae
140° C, 8 MPa H_2,
52 hr, 99% conv

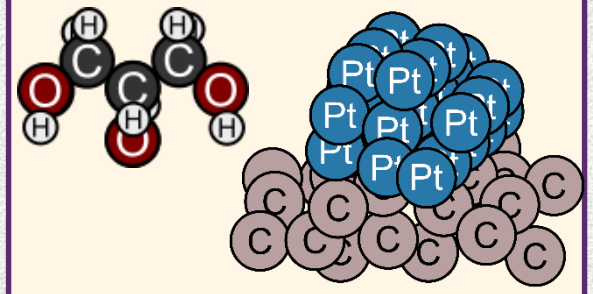


200 g of 1 wt. % gly/water, 200° C,
4MPa,0.1 g cat.(1:0.3 wt.%Au:Re),30hr

K. Tomishige, et al. ACS Catal, 2016, 6, 10, 6393

Hydrogenolysis of glycerol

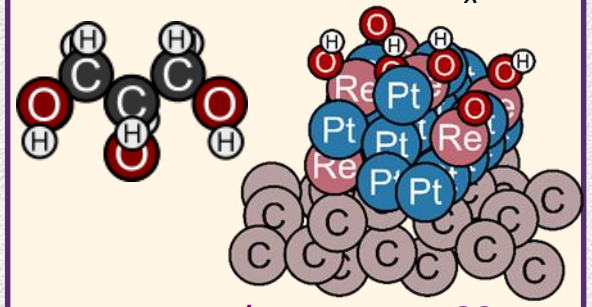
Glycerol on Pt



1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

Primary C–O cleavage
Some C–C cleavage

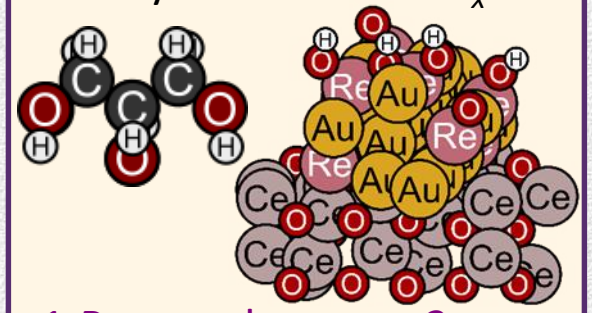
Glycerol on $PtReO_x$



1-Propanol	169
1,2-Propanediol	137
2-Propanol	71
1,3-Propanediol	25
Ethylene glycol	0
Methanol	0
Gases	1

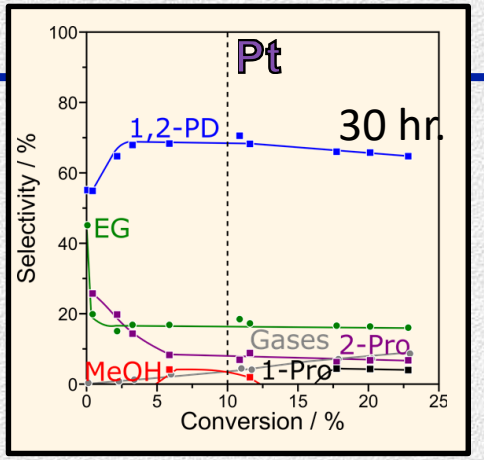
Reaction rate increased
Primary C–O increased
Negligible C–C
Facilitates secondary C–O

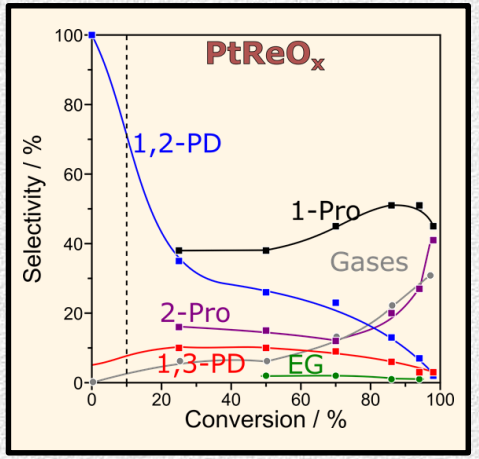
Glycerol on $AuReO_x$

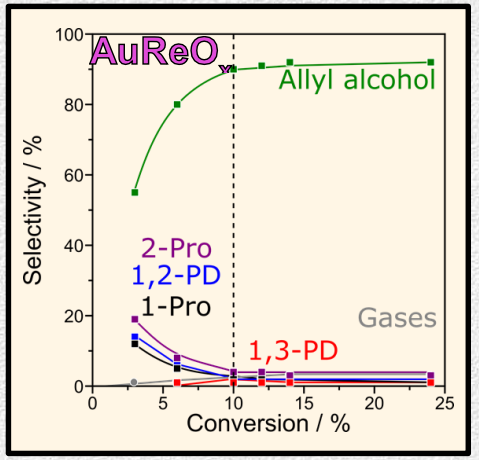


1-Propanol	2
1,2-Propanediol	2
2-Propanol	1
1,3-Propanediol	2
Ethylene glycol	0
Methanol	0
Gases	1
Allyl alcohol	101

Rates $PtReO_x$>$AuReO_x$>Pt
Negligible C–C cleavage
Increased C–O cleavage
unsaturated



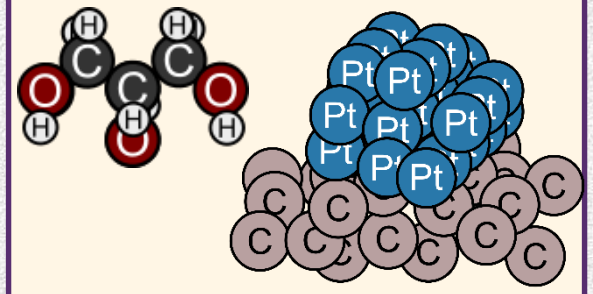




UF UNIVERSITY of FLORIDA

Hydrogenolysis of alcohols

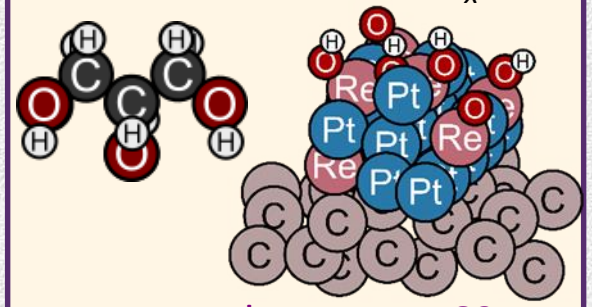
Glycerol on Pt



1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

Primary C–O cleavage
Some C–C cleavage

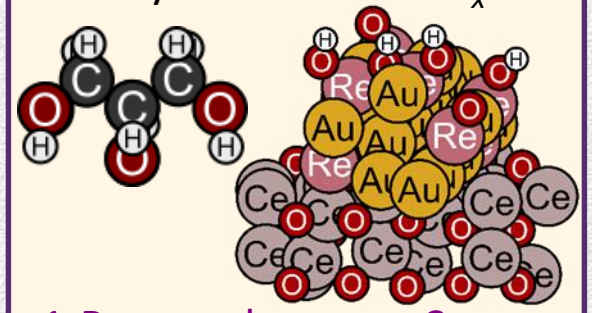
Glycerol on $PtReO_x$



1-Propanol	169
1,2-Propanediol	137
2-Propanol	71
1,3-Propanediol	25
Ethylene glycol	0
Methanol	0
Gases	1

Reaction rate increased
Primary C–O increased
Negligible C–C
Facilitates secondary C–O

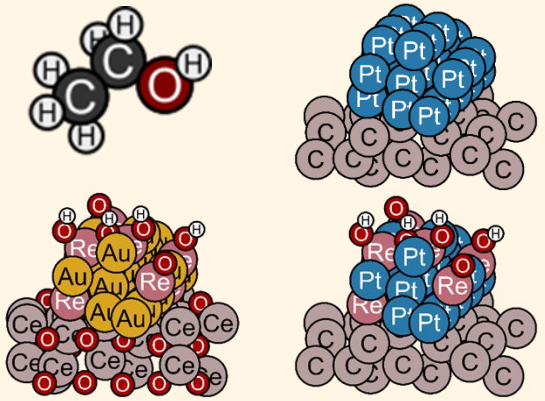
Glycerol on $AuReO_x$



1-Propanol	2
1,2-Propanediol	2
2-Propanol	1
1,3-Propanediol	2
Ethylene glycol	0
Methanol	0
Gases	1
Allyl alcohol	101

Rates $PtReO_x$>$AuReO_x$>Pt
Negligible C–C cleavage
Increased C–O cleavage
unsaturated

Ethanol



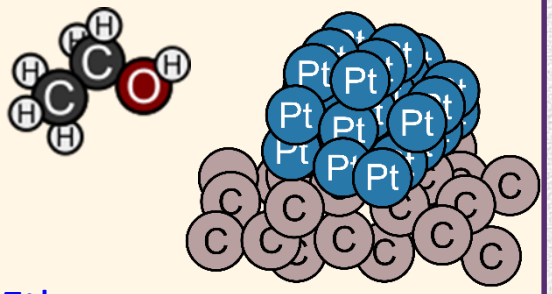
Ethanol
C–C bonds
Primary C–O
Volatile

Ideal for gas phase reaction

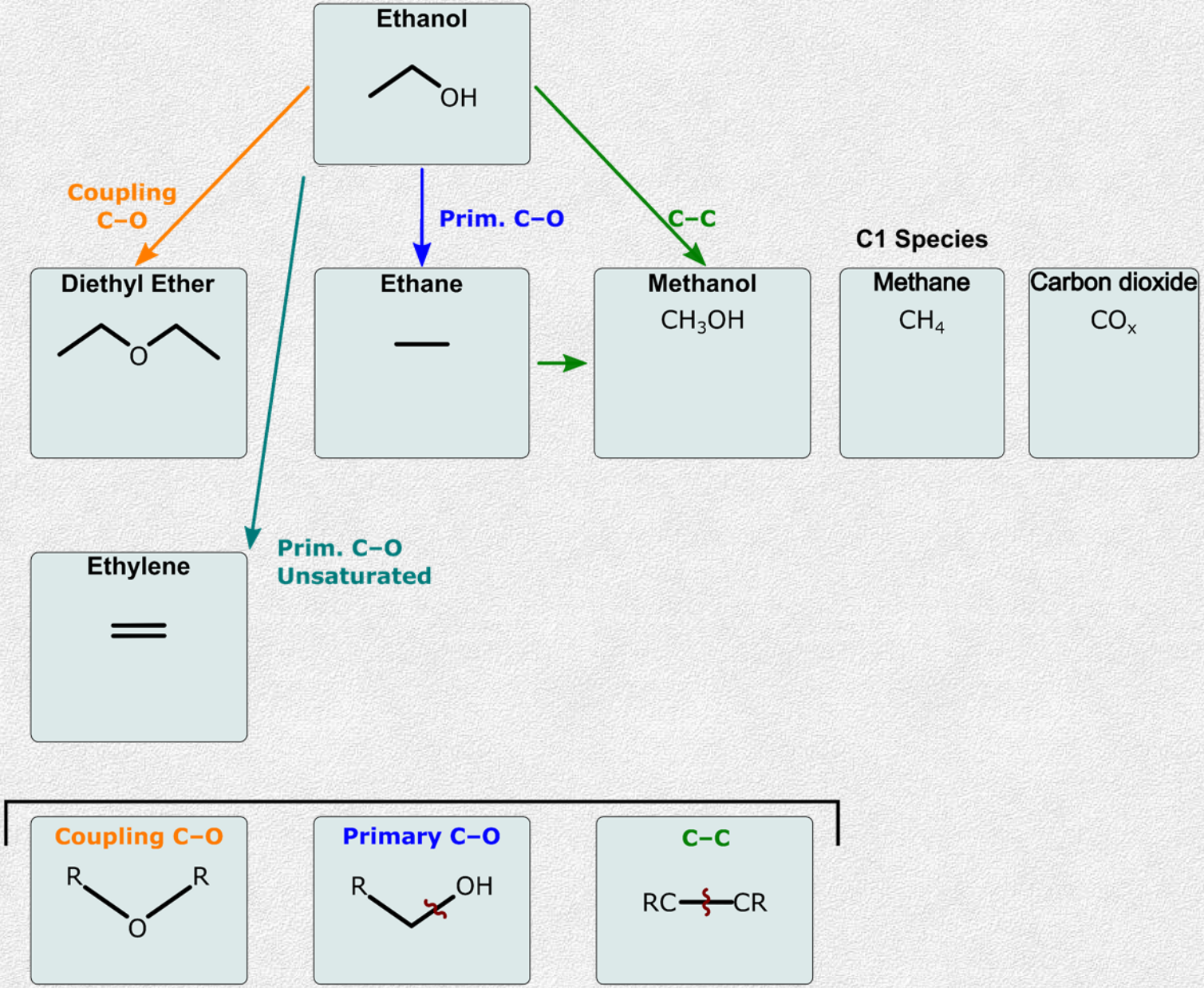
Test effects of water

Hydrogenolysis of ethanol

Ethanol (aq.) on Pt

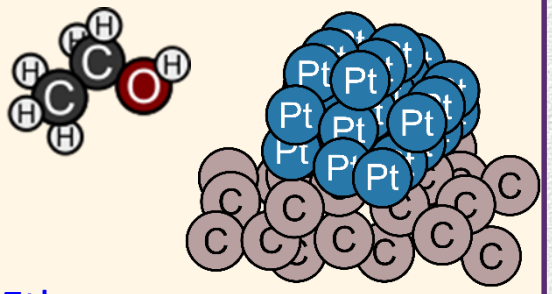


Ethane
Methanol
Methane
Carbon oxides
Diethyl ether
Ethylene

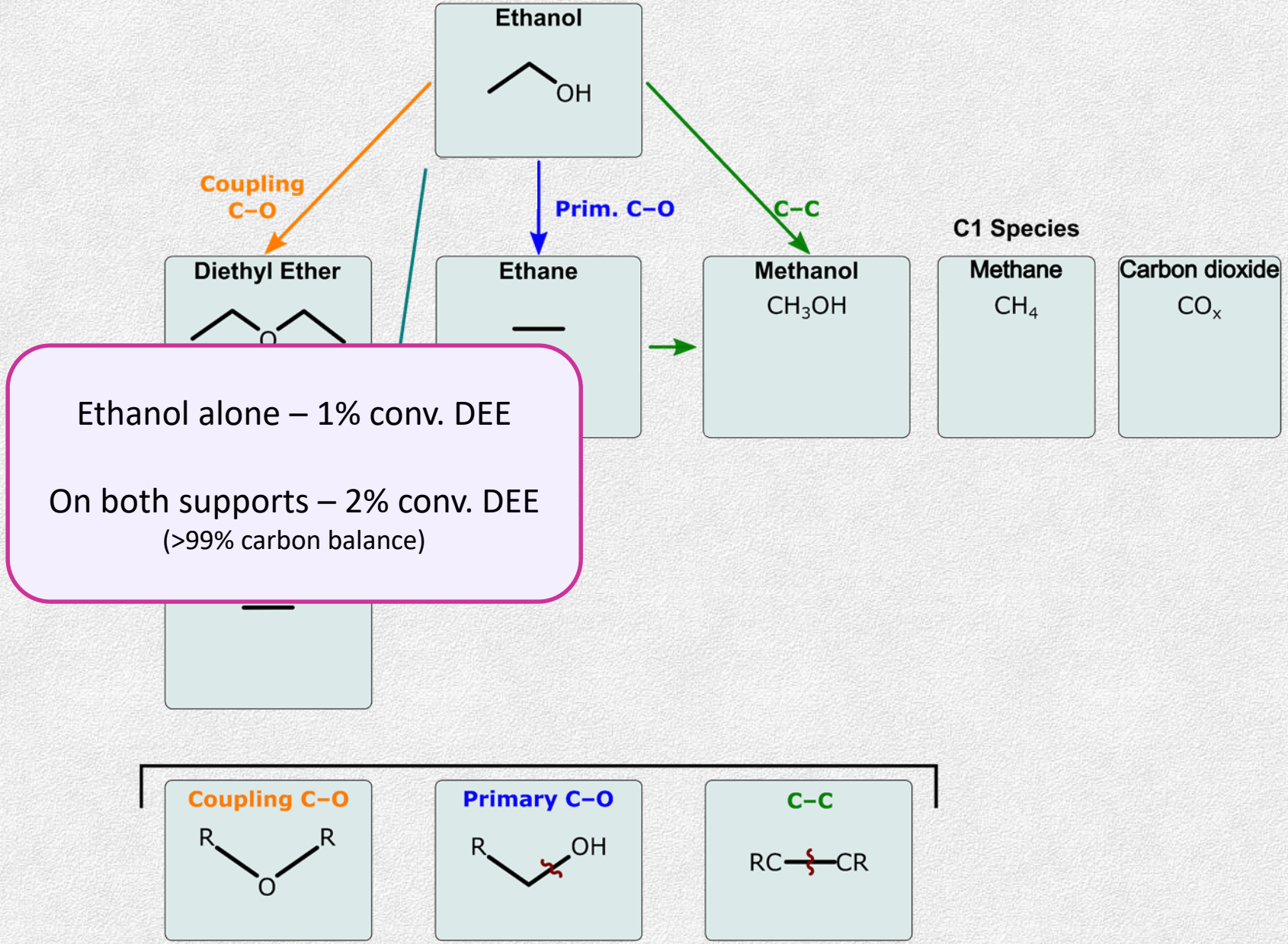


Hydrogenolysis of ethanol

Ethanol (aq.) on Pt

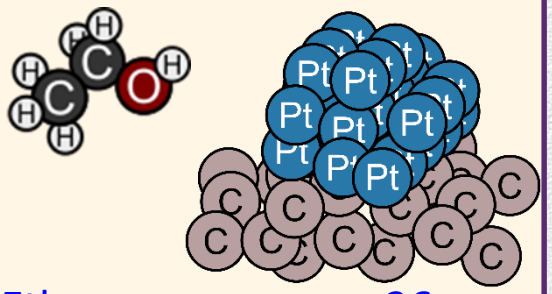


Ethane
Methanol
Methane
Carbon oxides
Diethyl ether
Ethylene



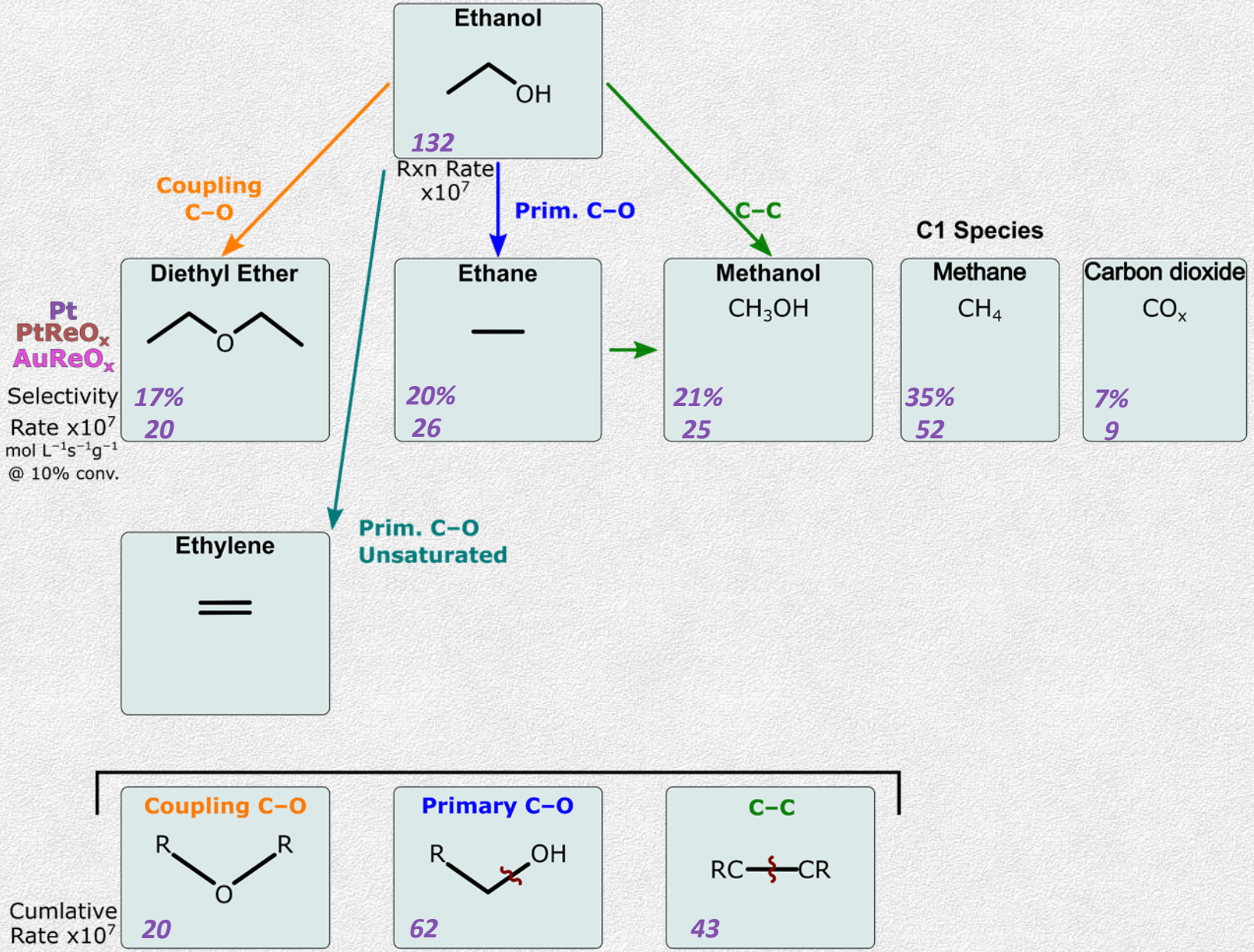
Hydrogenolysis…ethanol on Pt

Ethanol (aq.) on Pt



Ethane	26
Methanol	25
Methane	52
Carbon oxides	9
Diethyl ether	20

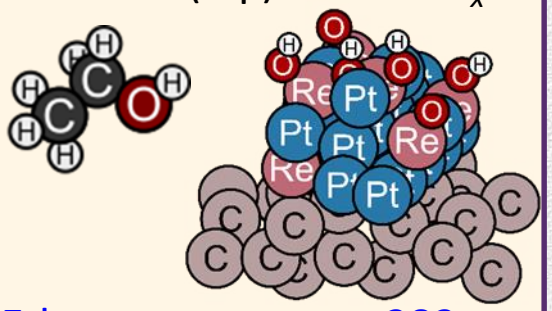
Ethanol rates > glycerol
Methane main product



200 g of 1 wt. % EtOH/water, 200° C, 4 MPa, 0.1 g cat.(5 wt.% Pt),30hr

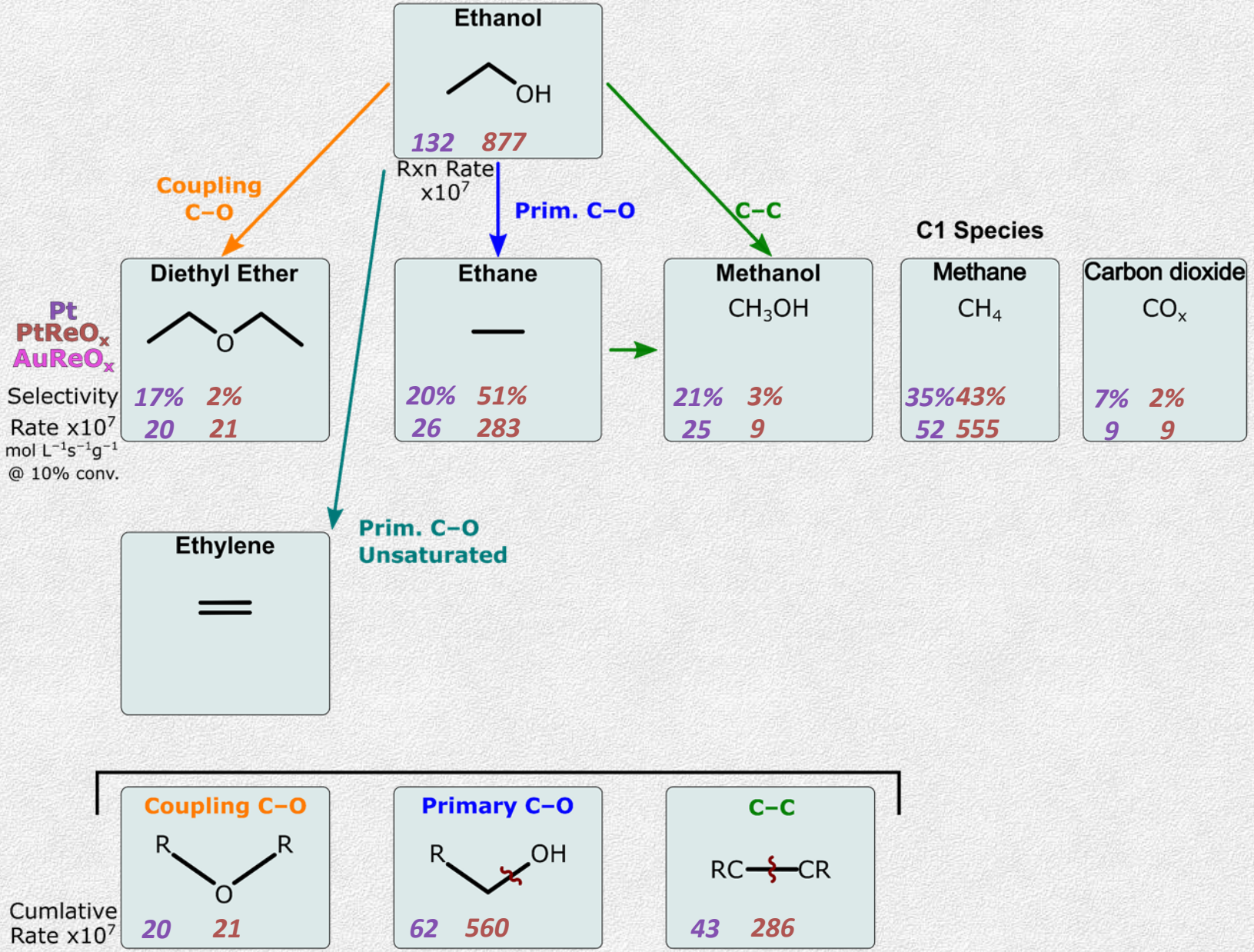
Hydrogenolysis…ethanol on $PtReO_x$

Ethanol (aq.) on $PtReO_x$



Ethane	283
Methanol	9
Methane	555
Carbon oxides	9
Diethyl ether	21

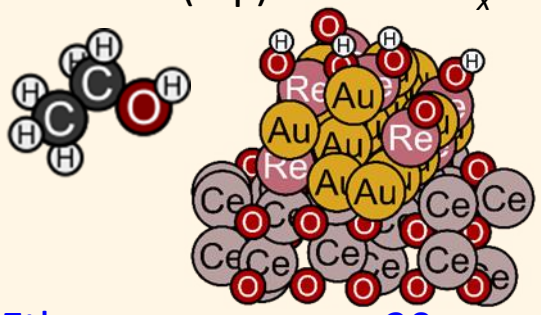
Reaction rate × 7
Enhanced C–O × 11
C–O Coupling same



200 g of 1 wt. % EtOH/water, 200° C, 4 MPa, 0.1 g cat.(5 wt.% Pt&Re),30hr

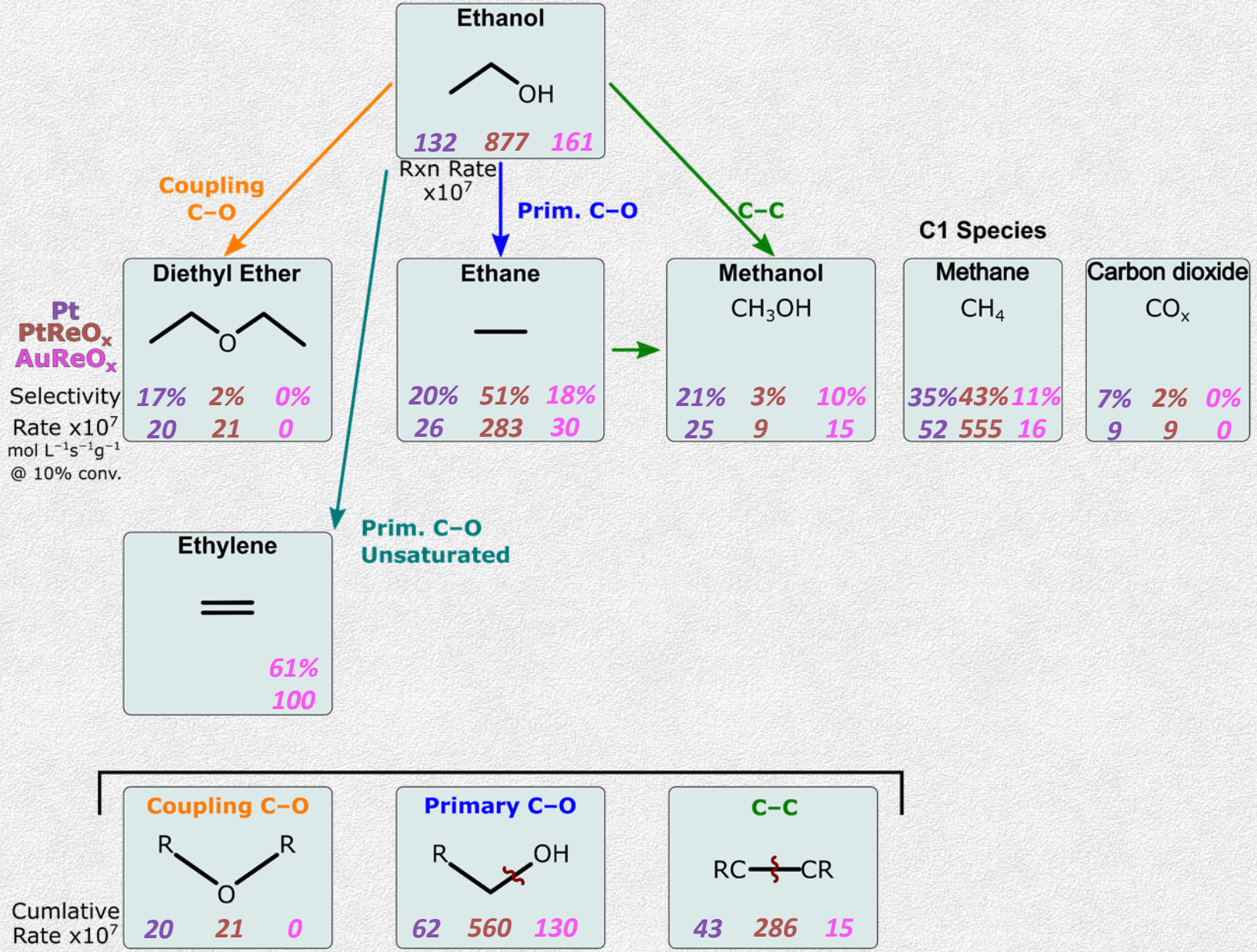
Hydrogenolysis…ethanol on $AuReO_x$

Ethanol (aq.) on $AuReO_x$



Ethane	30
Methanol	15
Methane	16
Carbon oxides	0
Diethyl ether	0
Ethylene	100

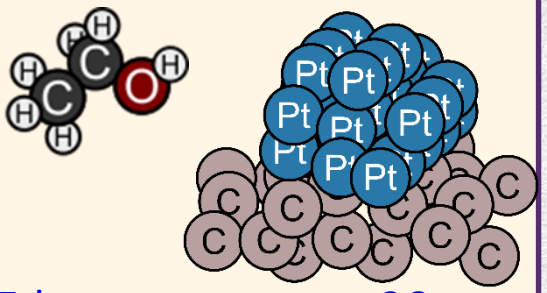
Rates $PtReO_x$>$AuReO_x$>Pt
C–O coupling eliminated
Unsaturated C–O



200 g of 1 wt. % gly/water, 200° C, 4MPa,0.1 g cat.(1:0.3 wt.%Au:Re),30hr

Hydrogenolysis of ethanol

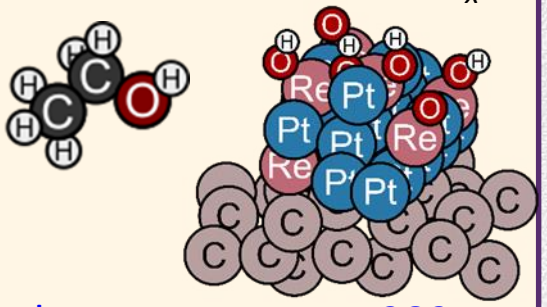
Ethanol (aq.) on Pt



Ethane	26
Methanol	25
Methane	52
Carbon oxides	9
Diethyl ether	20

Ethanol rates > glycerol
Methane main product

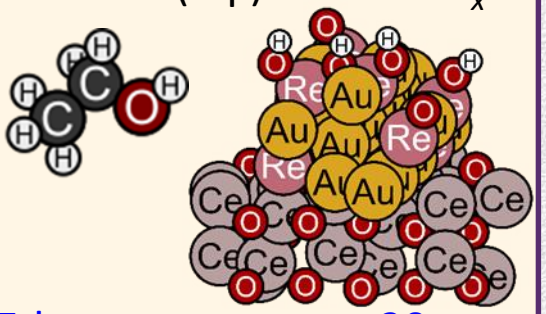
Ethanol (aq.) on $PtReO_x$



Ethane	283
Methanol	9
Methane	555
Carbon oxides	9
Diethyl ether	21

Reaction rate × 7
Enhanced C–O × 11
C–O Coupling same

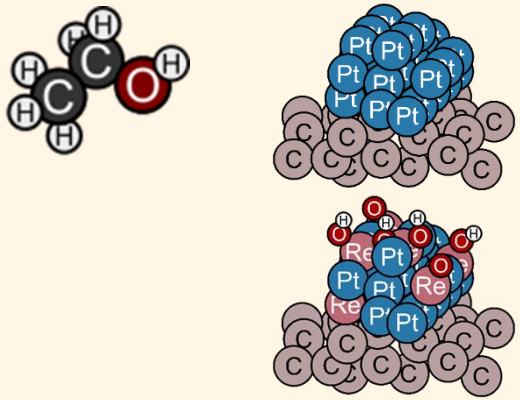
Ethanol (aq.) on $AuReO_x$



Ethane	30
Methanol	15
Methane	16
Carbon oxides	0
Diethyl ether	0
Ethylene	100

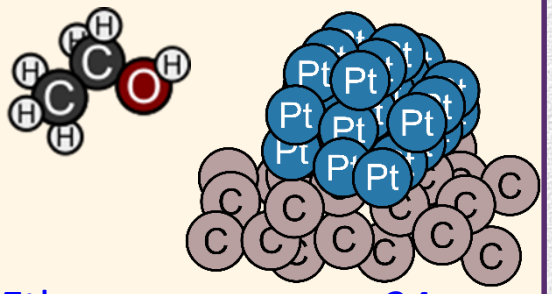
Rates $PtReO_x$>$AuReO_x$>Pt
C–O coupling eliminated
Unsaturated C–O

Ethanol gas phase



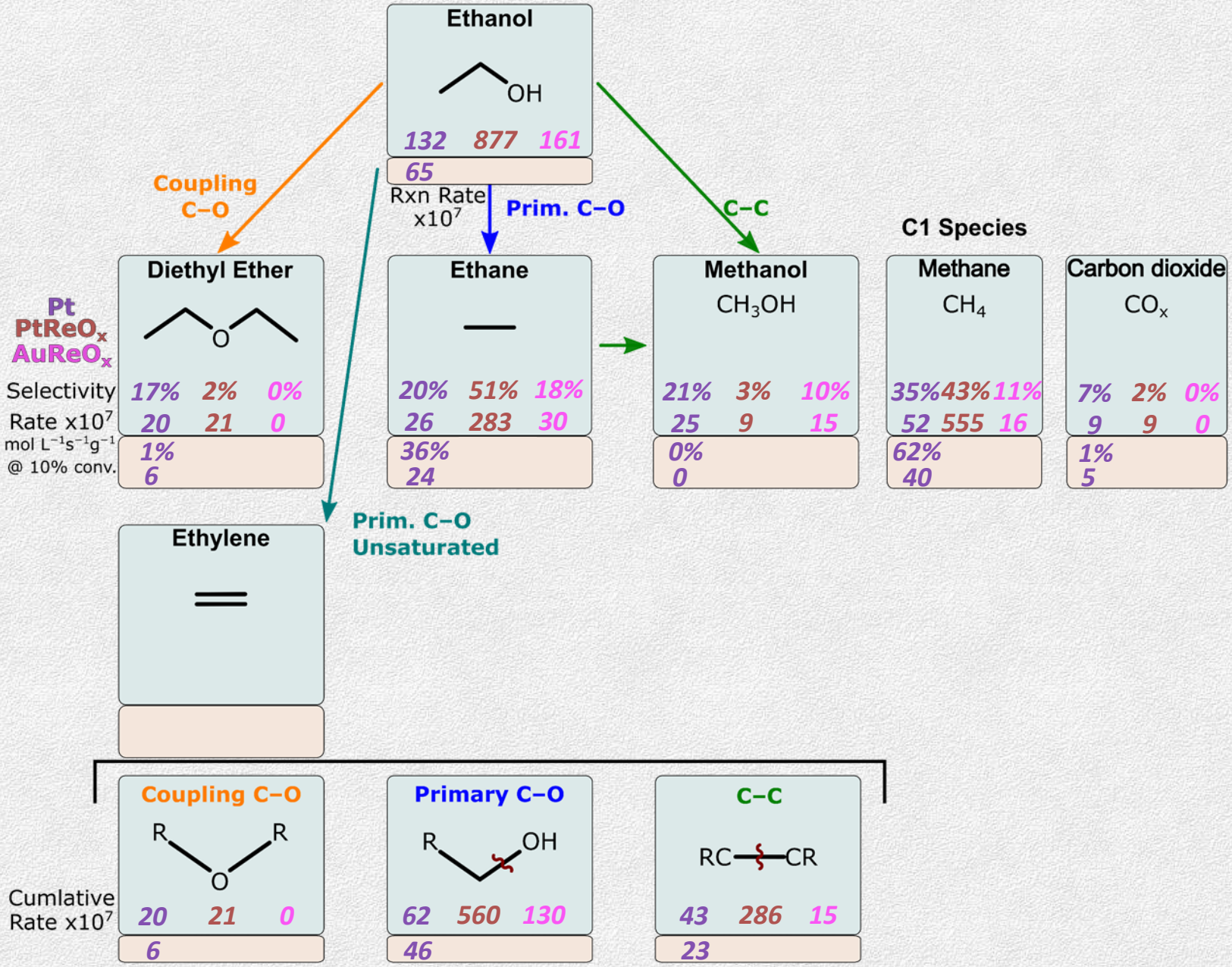
Hydrogenolysis…ethanol vapor on Pt

Ethanol (g) on Pt



Ethane	24
Methanol	0
Methane	40
Carbon oxides	5
Diethyl ether	6

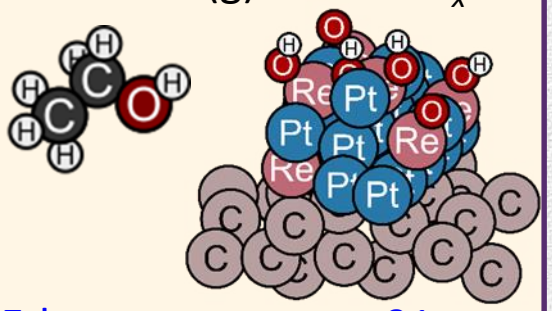
Gas reaction slower
No methanol



107 SCCM, EtOH:H_2=0.003, 215° C, 2 MPa, 0.1 g cat.(5 wt.% Pt)

Hydrogenolysis…ethanol vapor on $PtReO_x$

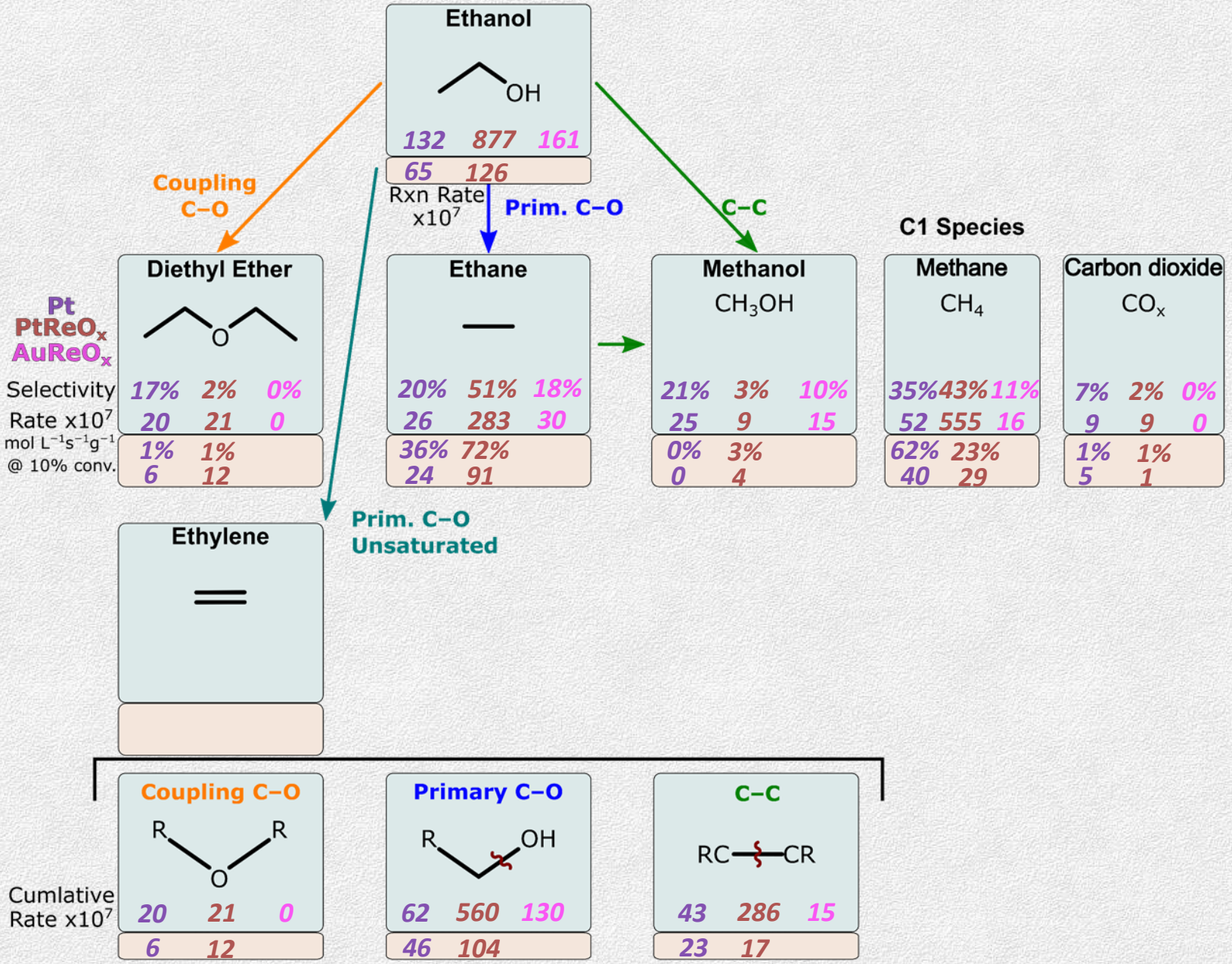
Ethanol (g) on $PtReO_x$



Ethane	91
Methanol	4
Methane	29
Carbon oxides	1
Diethyl ether	12

Reaction rate × 2

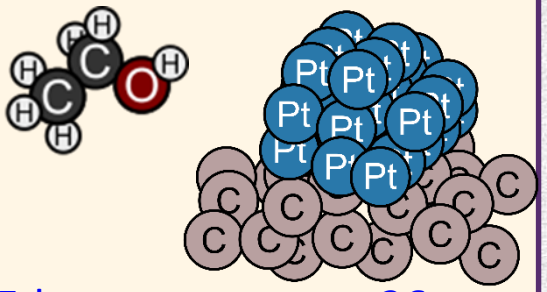
C–O cleavage > C–C



107 SCCM, EtOH:H_2=0.003, 215° C, 2 MPa, 0.1 g cat.(5 wt.% Pt&Re)

Aqueous vs gas phase

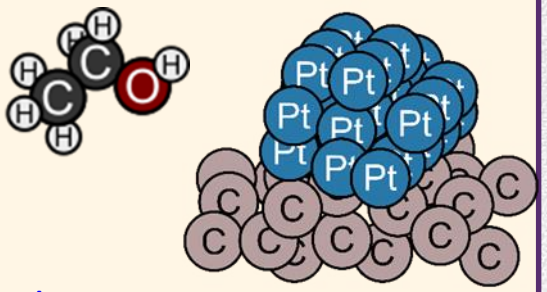
Ethanol (aq.) on Pt



Ethane	26
Methanol	25
Methane	52
Carbon oxides	9
Diethyl ether	20

Ethanol rates > glycerol
Methane main product

Ethanol (g) on Pt



Ethane	24
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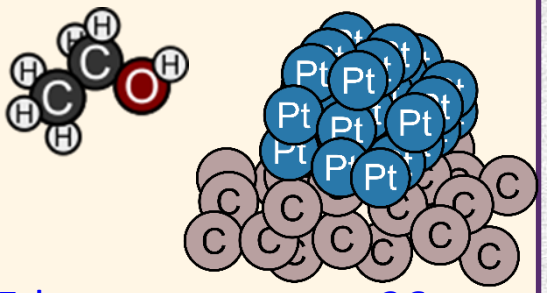
Methane	40
Carbon oxides	5
Diethyl ether	6

Gas reaction slower
No methanol

Aqueous vs gas phase

Ethanol (aq.) on Pt



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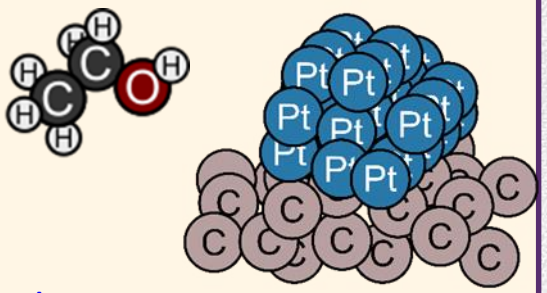
Diethyl ether	20

Ethanol rates > glycerol
Methane main product

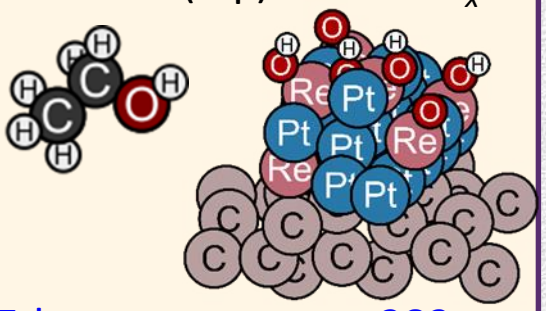
Ethanol (g) on Pt



Ethane	24
Methanol	0
Methane	40
Carbon oxides	5
Diethyl ether	6

Gas reaction slower
No methanol

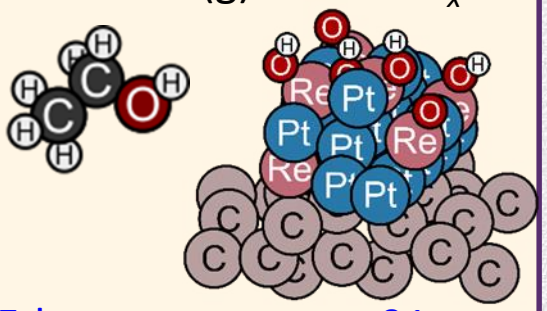
Ethanol (aq.) on $PtReO_x$



Ethane	283
Methanol	9
Methane	555
Carbon oxides	9
Diethyl ether	21

Reaction rate × 7 (Pt)
Enhanced C–O × 11
C–O Coupling same

Ethanol (g) on $PtReO_x$

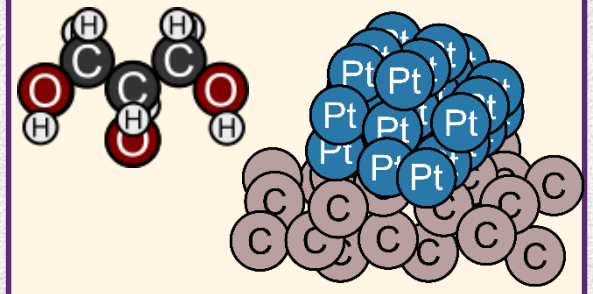


Ethane	91
Methanol	4
Methane	29
Carbon oxides	1
Diethyl ether	12

Reaction rate × 2 (Pt)
Reaction rate × 2 (aq.)
C–O cleavage > C–C

Hydrogenolysis of glycerol

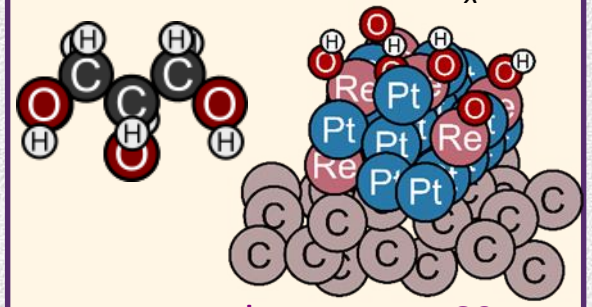
Glycerol on Pt



1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

Primary C–O cleavage
Some C–C cleavage

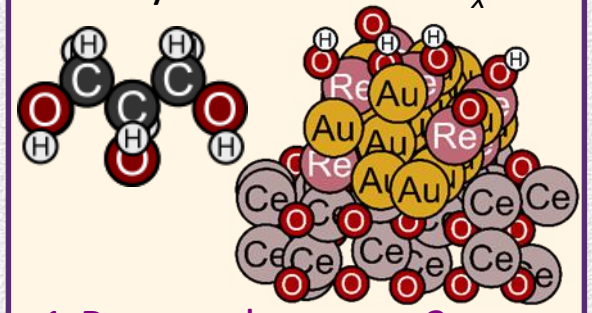
Glycerol on $PtReO_x$



1-Propanol	169
1,2-Propanediol	137
2-Propanol	71
1,3-Propanediol	25
Ethylene glycol	0
Methanol	0
Gases	1

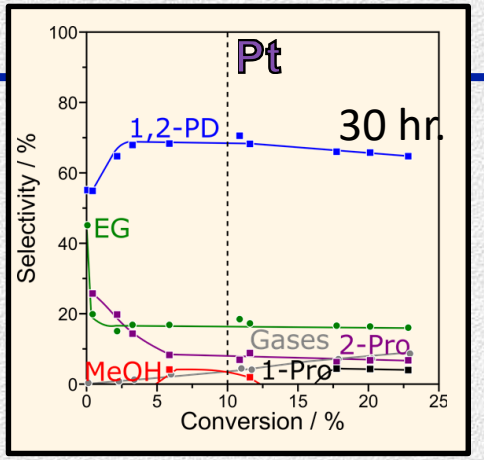
Reaction rate increased
Primary C–O increased
Negligible C–C
Facilitates secondary C–O

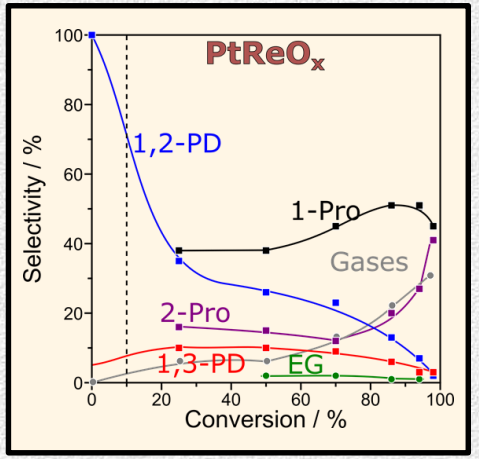
Glycerol on $AuReO_x$

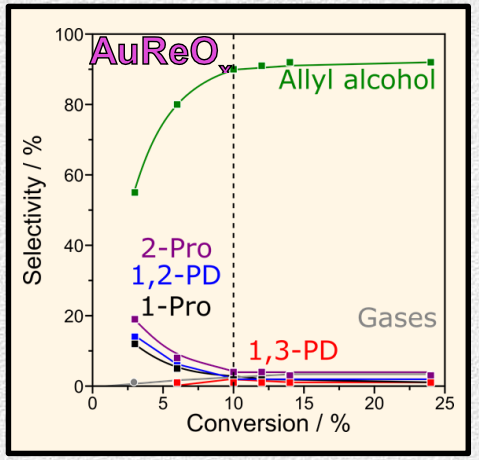


1-Propanol	2
1,2-Propanediol	2
2-Propanol	1
1,3-Propanediol	2
Ethylene glycol	0
Methanol	0
Gases	1
Allyl alcohol	101

Rates $PtReO_x$>$AuReO_x$>Pt
Negligible C–C cleavage
Increased C–O cleavage
unsaturated

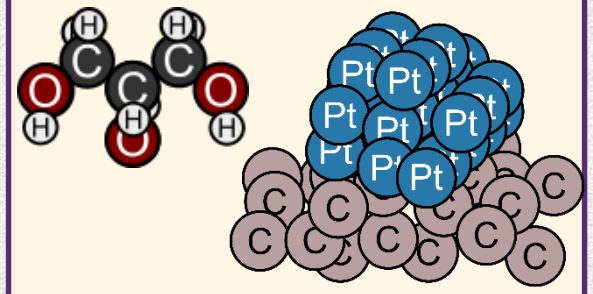






Future work

Glycerol on Pt



1,2-Propanediol	13
2-Propanol	3
Ethylene glycol	4
Methanol	1.5
Gases	1.5

Primary C–O cleavage
Some C–C cleavage

Glycerol on $PtReO_x$

unsaturated

Glycerol on $AuReO_x$

Perform flow reactions with more conditions

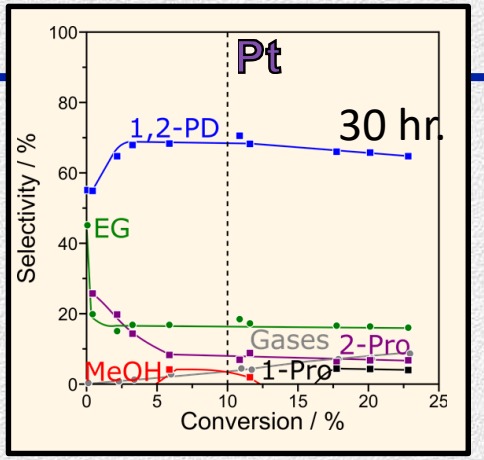
(Run reactions with ethanol/water (g) mixtures)

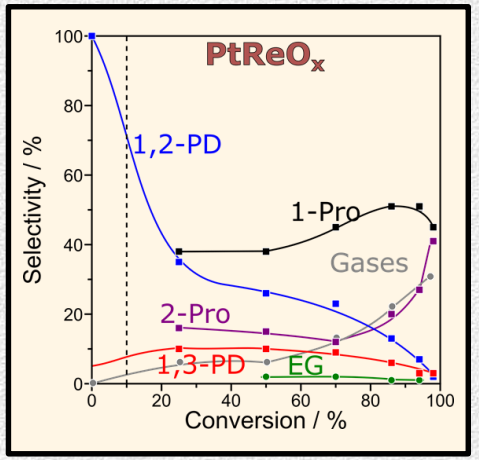
Use titrating base in flow reactor

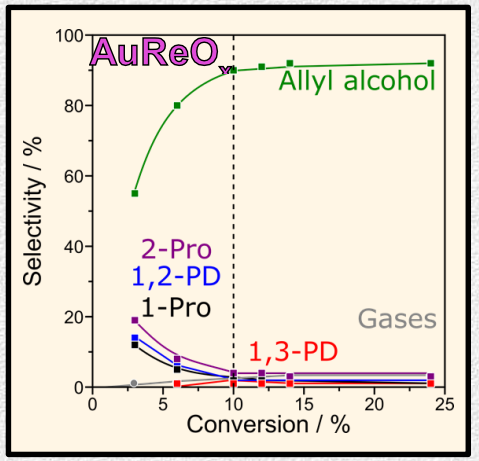
(Elucidate Brønsted acid theory)

Perform reactions with ethylene glycol

(Help identify intermediates)

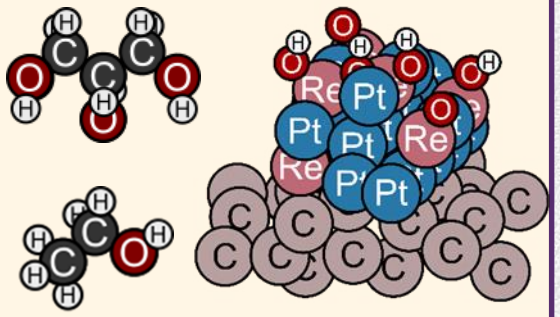






Recap

Alcohols on metals



Rates $PtReO_x$>$AuReO_x$>Pt

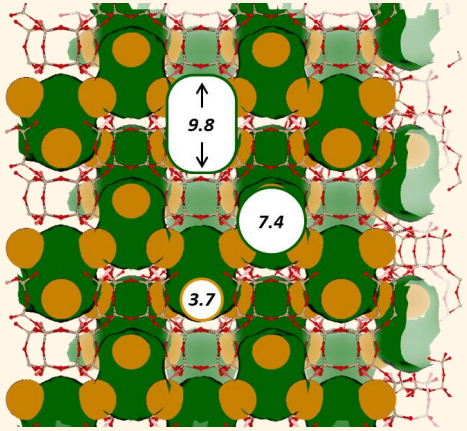
Rates ethanol > glycerol

ReO_x
Promotes 1°C–O cleavage
Facilitates 2°C–O cleavage
Reduces C–C cleavage

$AuReO_x$ produces unsaturated compounds

Alcohols in zeolites

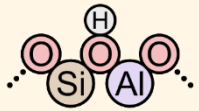
Aluminosilicates (Confinement)



Methanol dehydration

H 1+
O 2−
Si 4+
Al 3+

Brønsted acids

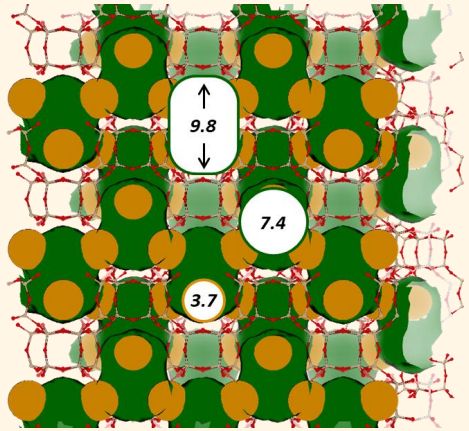


Energies in kJ mol^{-1}

The zeolite chabazite

Alcohols in zeolites

Aluminosilicates (Confinement)



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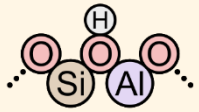
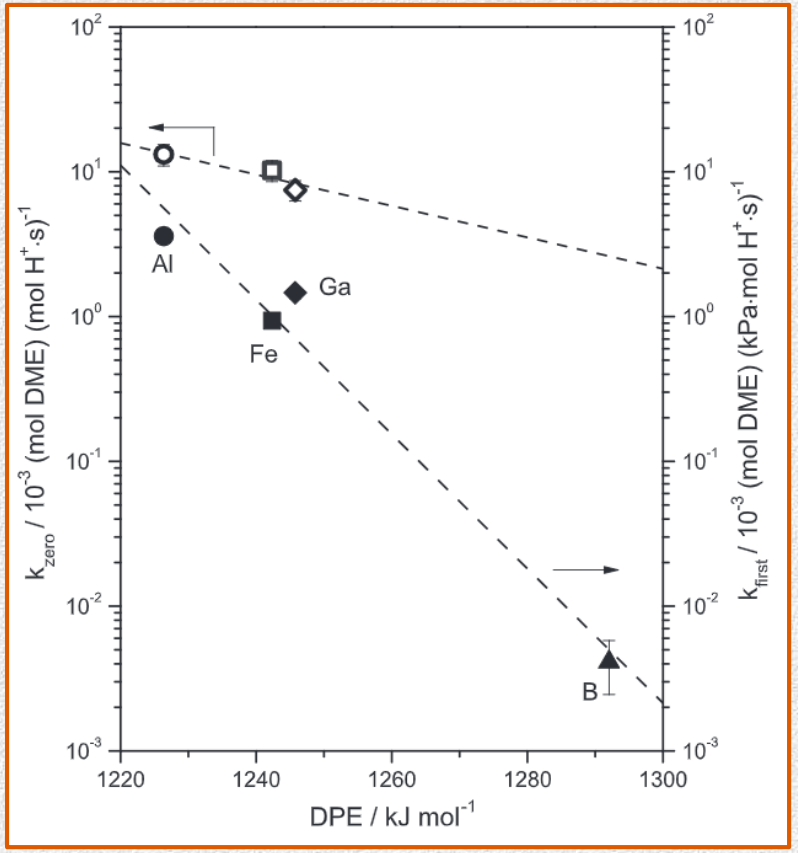
Brønsted acids



Determine acid strength

Rates trend with acidy

Examine methanol dehydration



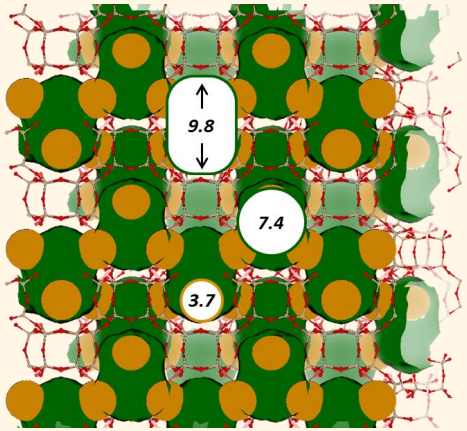
1 Crystallographically Unique T-site
4 O sites for H⁺

E. Iglesia, et al. Journal of Cat., 2014, 58

The zeolite chabazite

Alcohols in zeolites

Aluminosilicates
(Confinement)



Methanol dehydration

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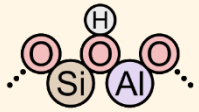
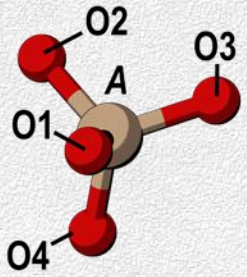
O 2−
Si 4+
Al 3+

Brønsted acids



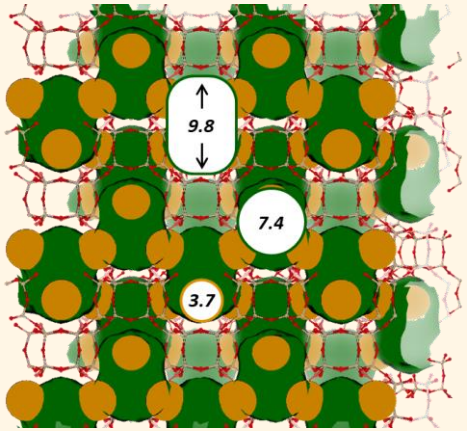


1 Crystallographically Unique T-site
4 O sites for H^+

The zeolite chabazite

Alcohols in zeolites

Aluminosilicates
(Confinement)



Methanol dehydration

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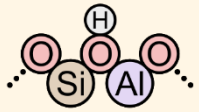
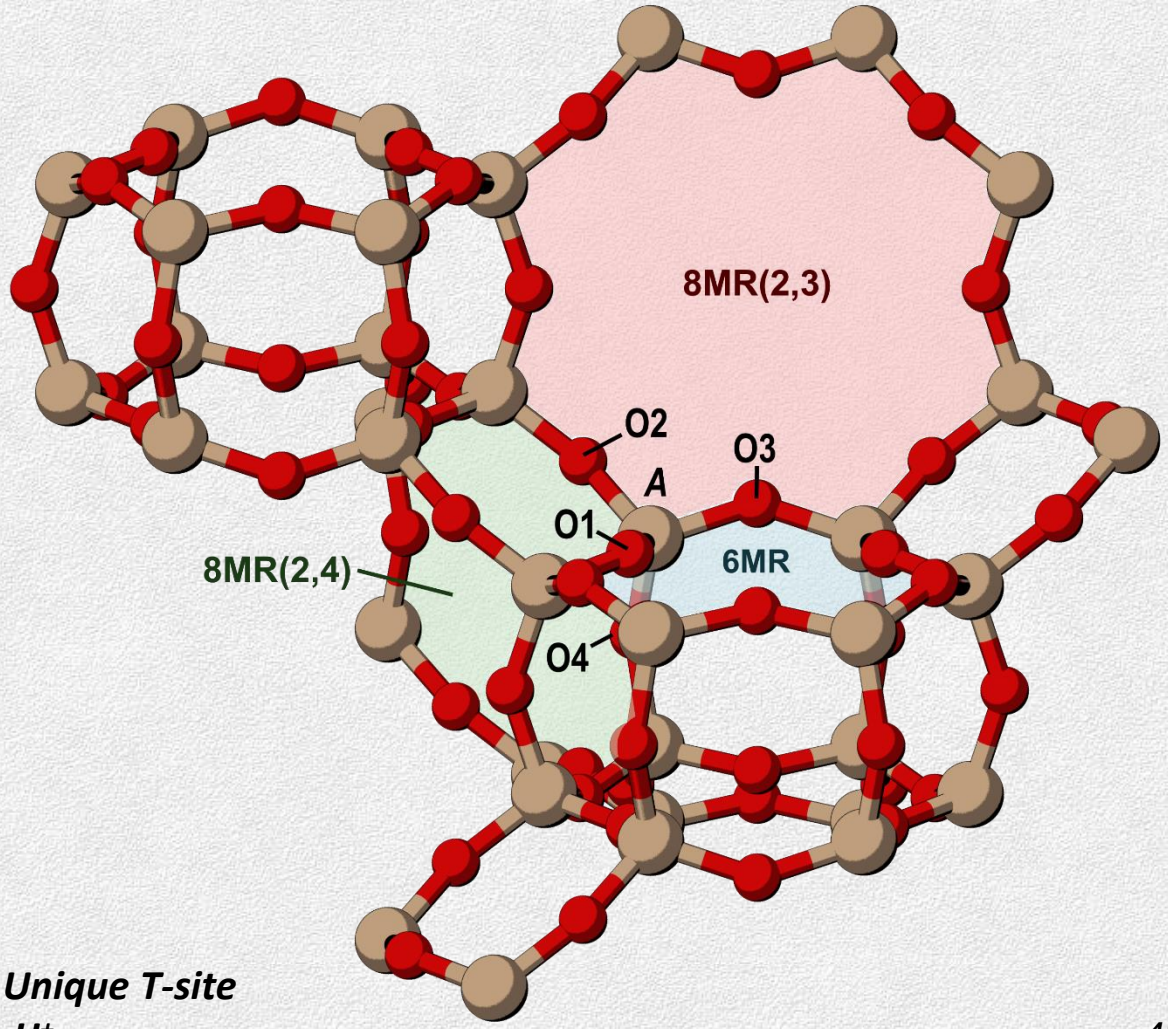
Brønsted acids



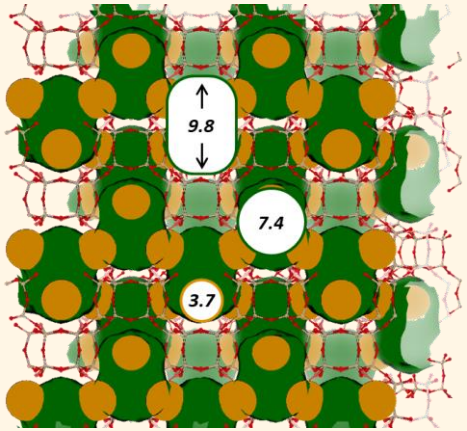


1 Crystallographically Unique T-site
4 O sites for H^+

The zeolite chabazite

Alcohols in zeolites

Aluminosilicates
(Confinement)



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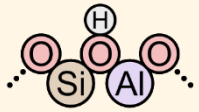
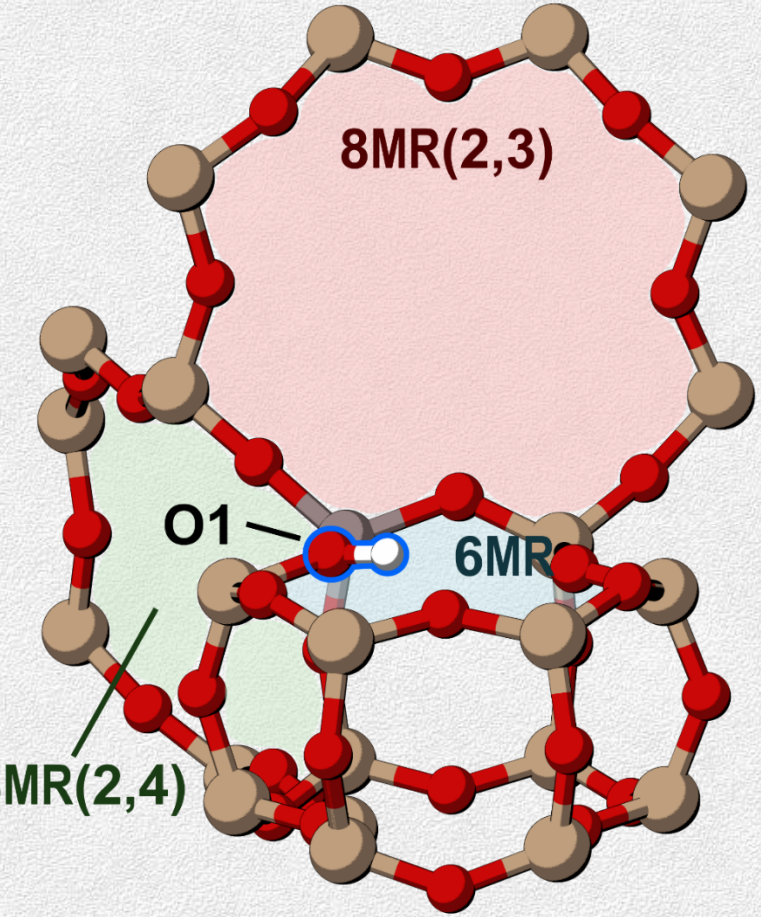




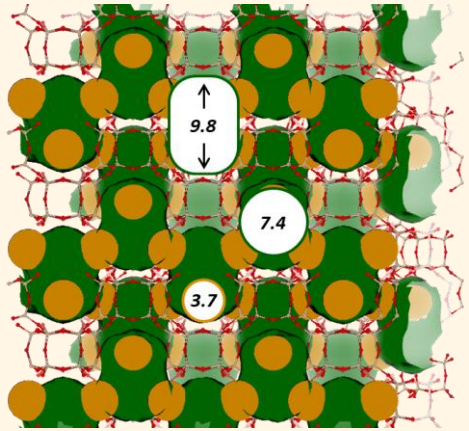
O1: ΔE_0: 0

1 Crystallographically Unique T-site
4 O sites for H^+

Brønsted acids in chabazite

Alcohols in zeolites

Aluminosilicates
(Confinement)



Methanol dehydration

H 1+
O 2−
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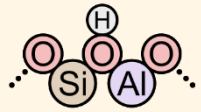
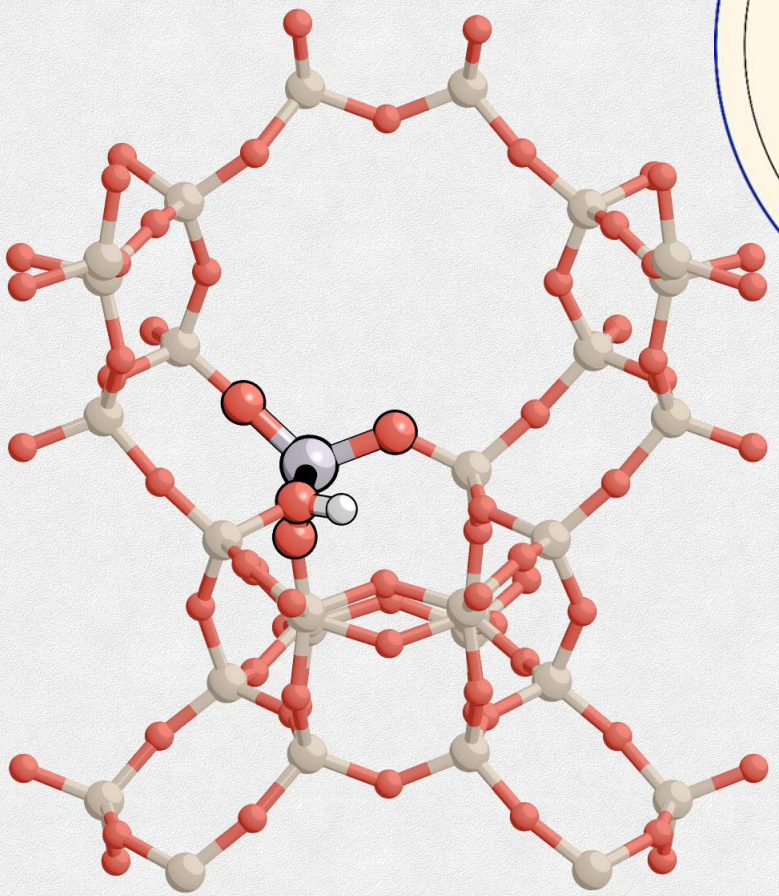
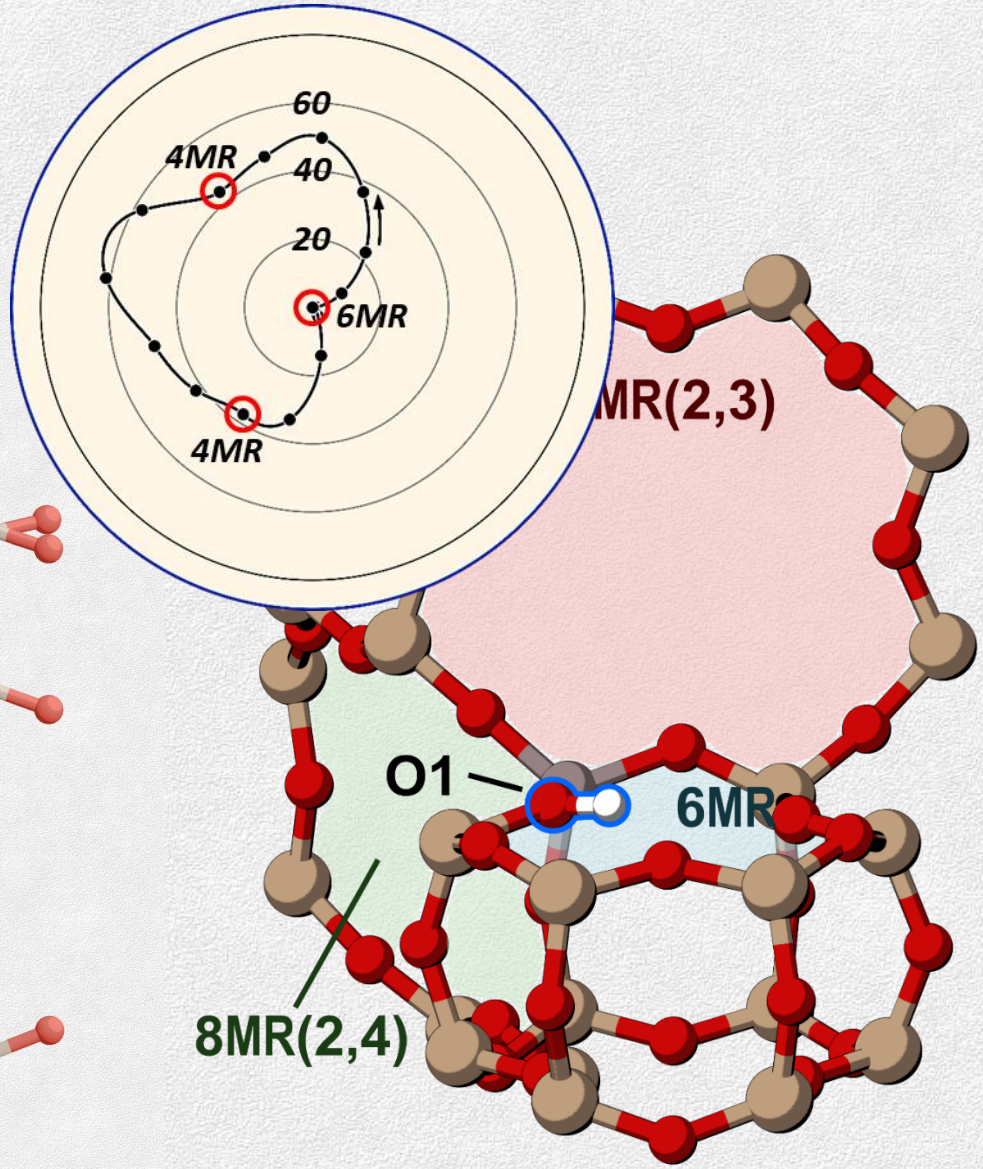
Brønsted acids





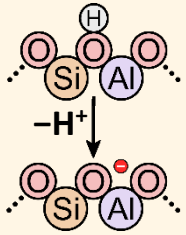


1 Crystallographically Unique T-site
4 O sites for H⁺

Energies in kJ mol⁻¹

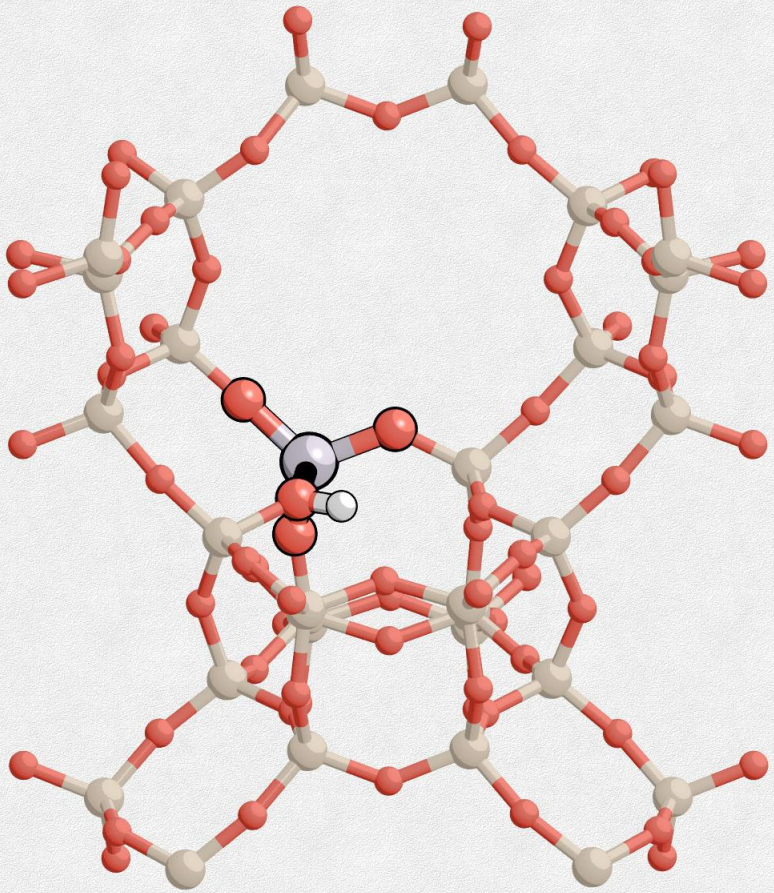
Brønsted acids in chabazite

DPE in CHA

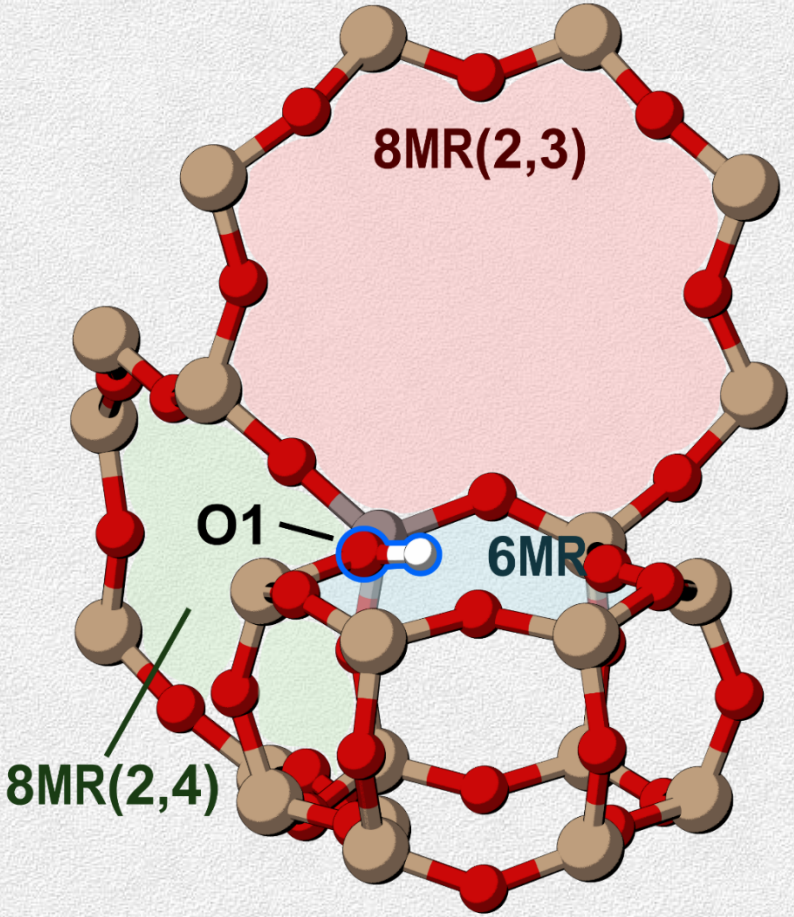


Isolated: 1568

DPE	Mono
O1	1569
O2	1559
O3	1566
O4	1567



1 Crystallographically Unique T-site
4 O sites for H+

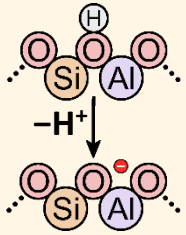


O1: ΔE_0: 0

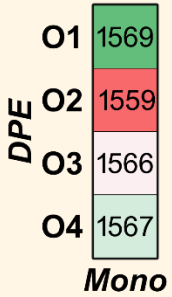
Energies in kJ mol^{-1}

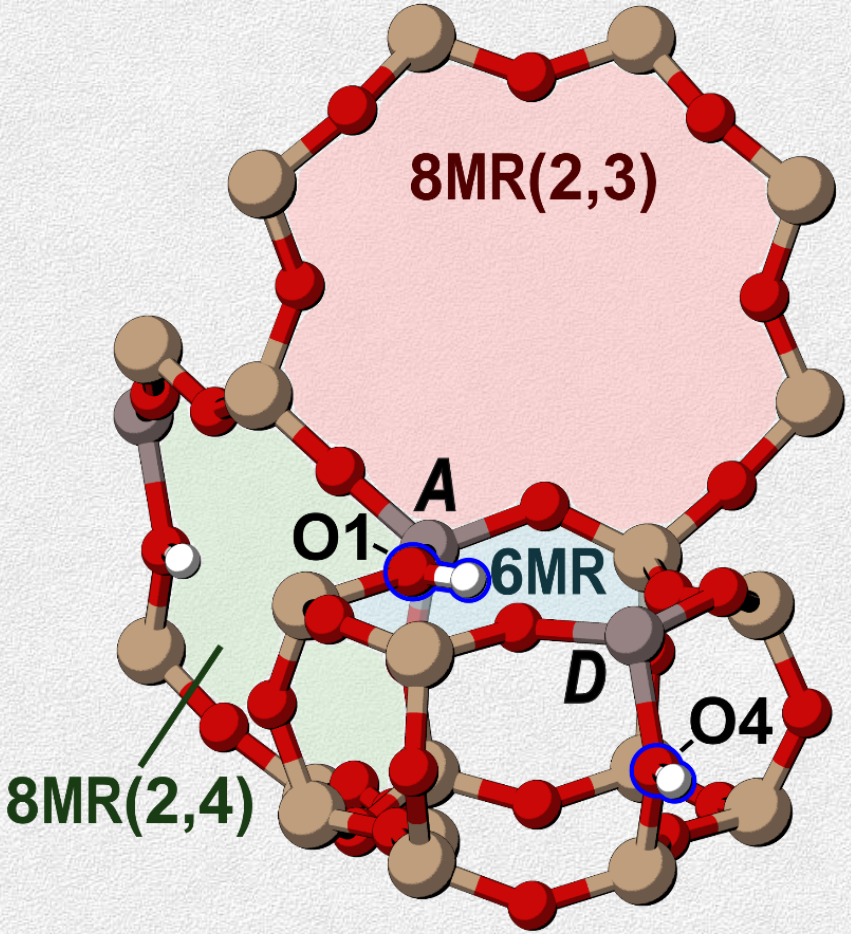
Paired Brønsted acids in chabazite

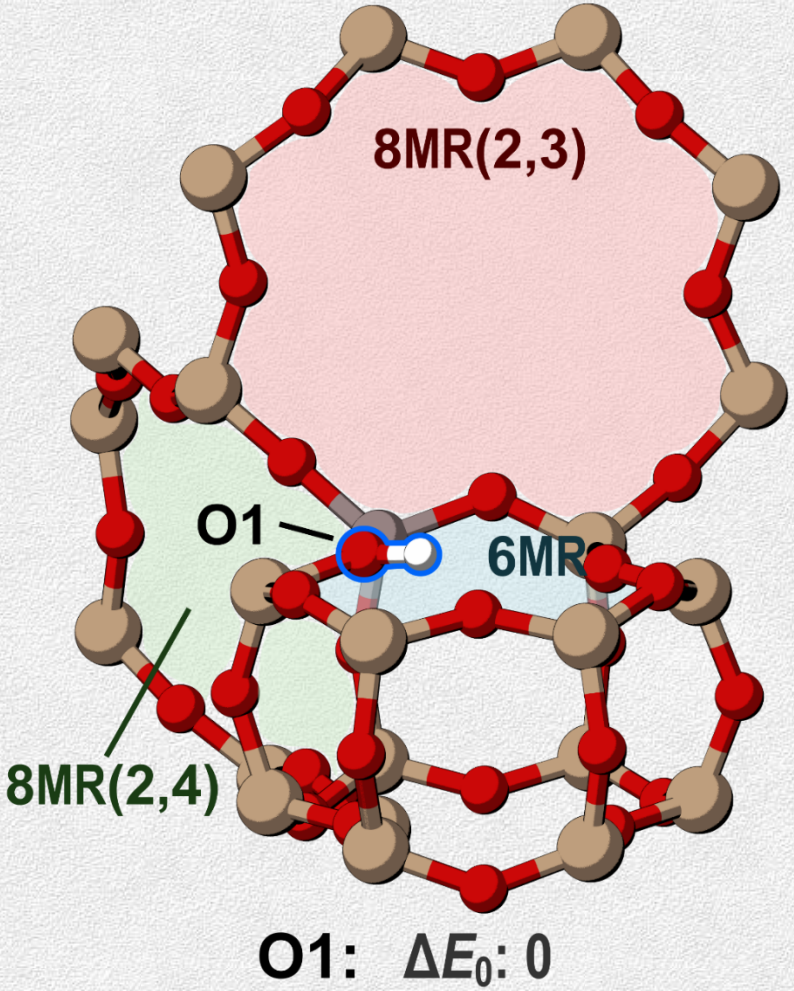
DPE in CHA



Isolated: 1568



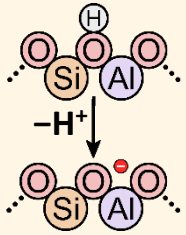




Energies in kJ mol^{-1}

Paired Brønsted acids in chabazite

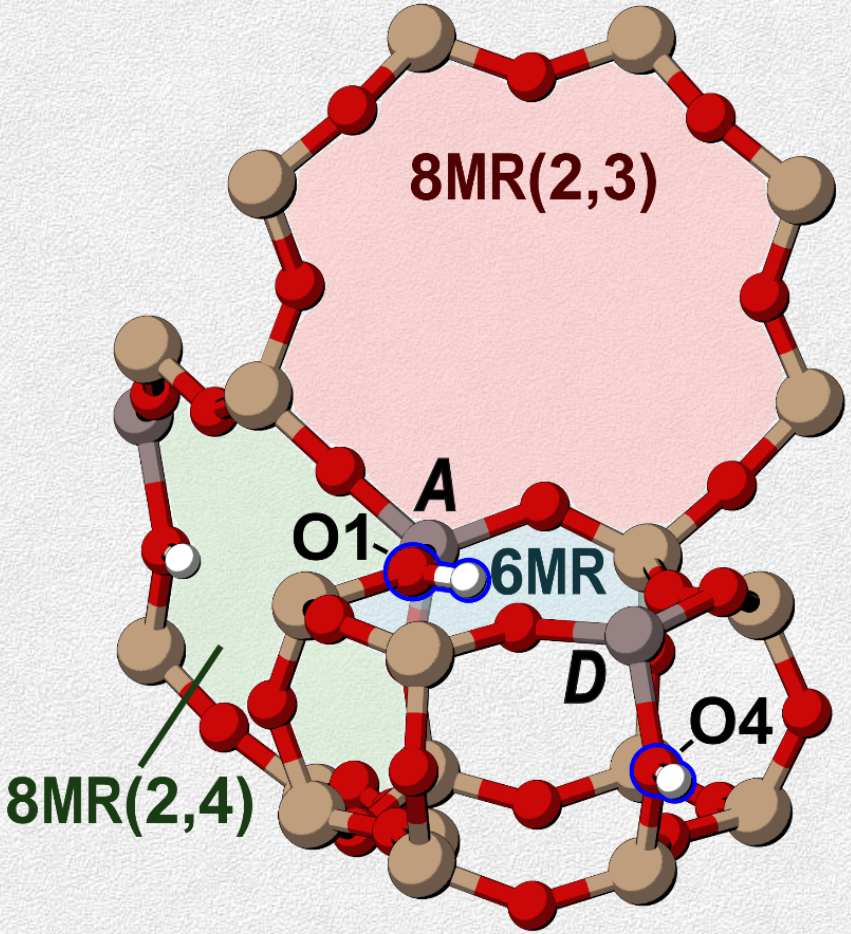
DPE in CHA

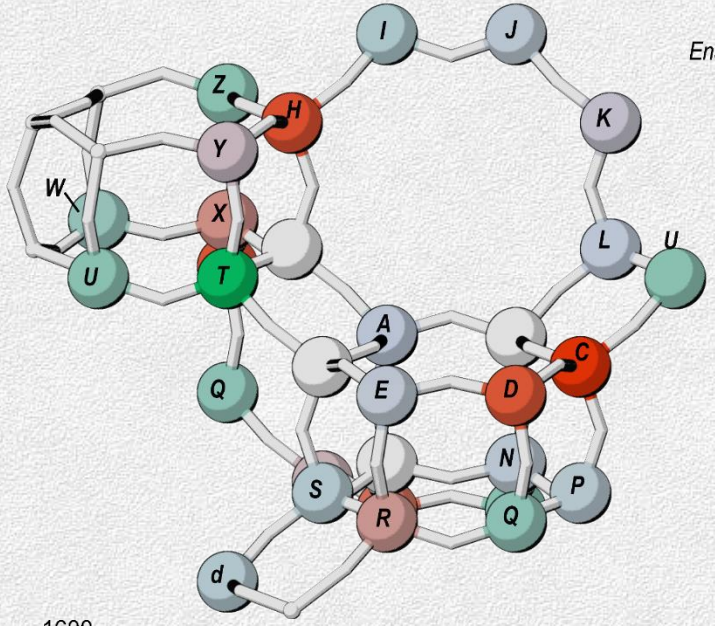


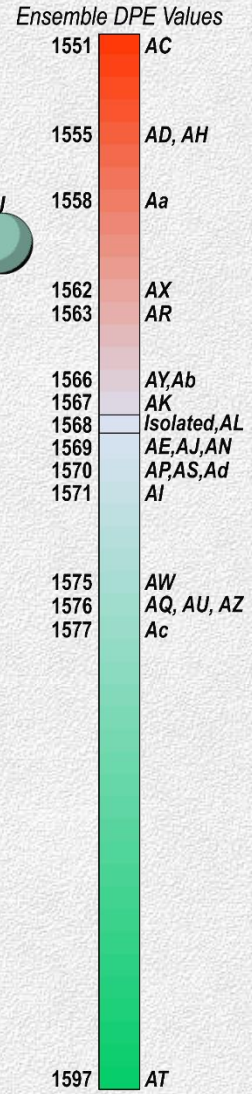
Isolated: 1568

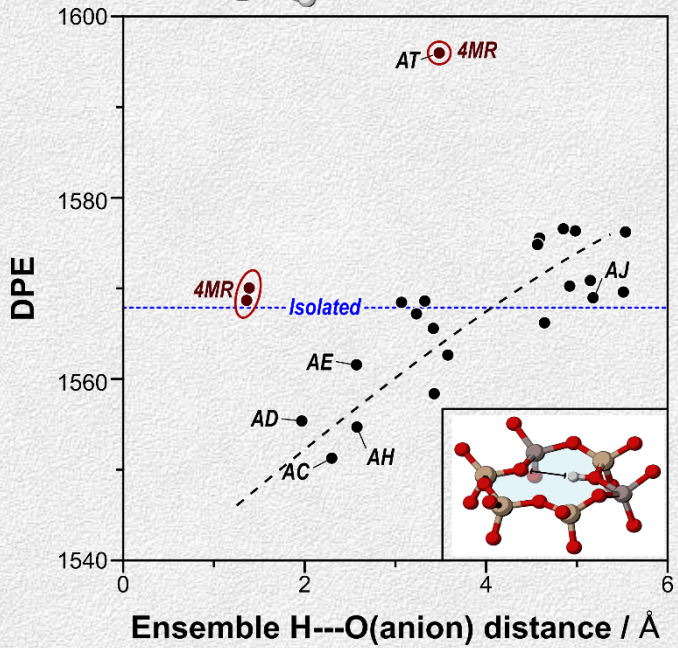
Paired: 1551–1597

DPE		Mono
O1	1569	
O2	1559	
O3	1566	
O4	1567	









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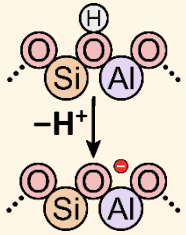
Energies in kJ mol^{-1}

Paired Brønsted acids in chabazite

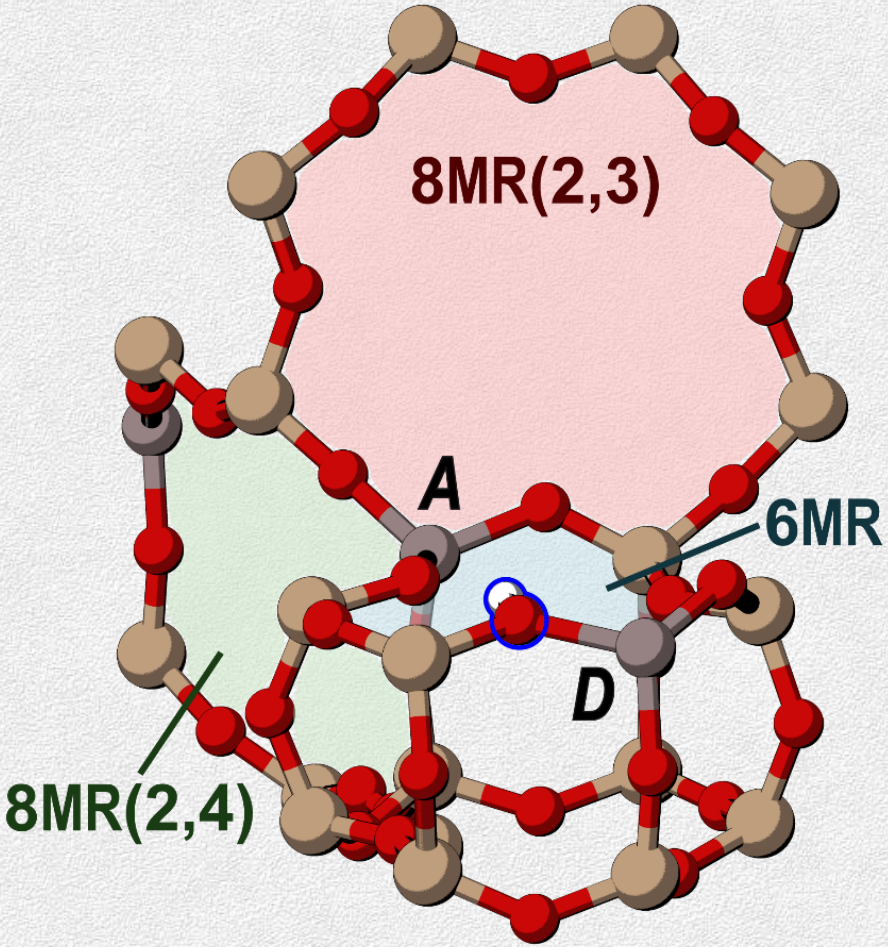
DPE in CHA

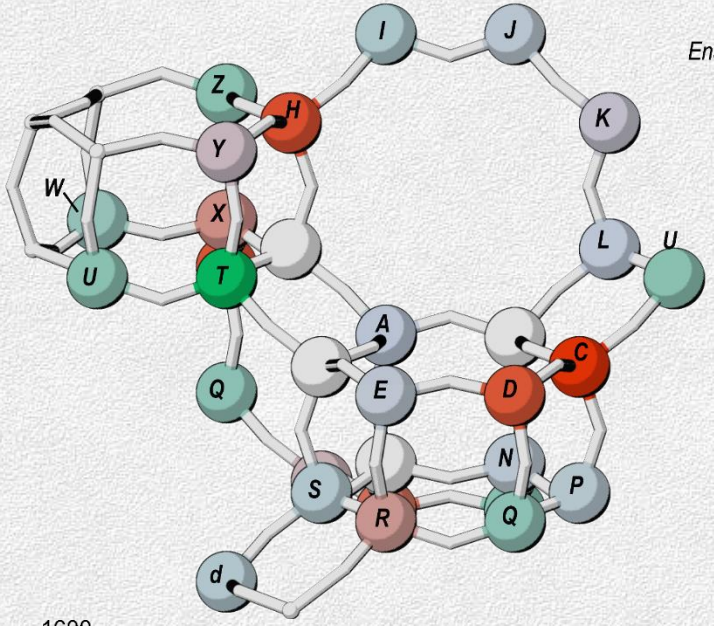


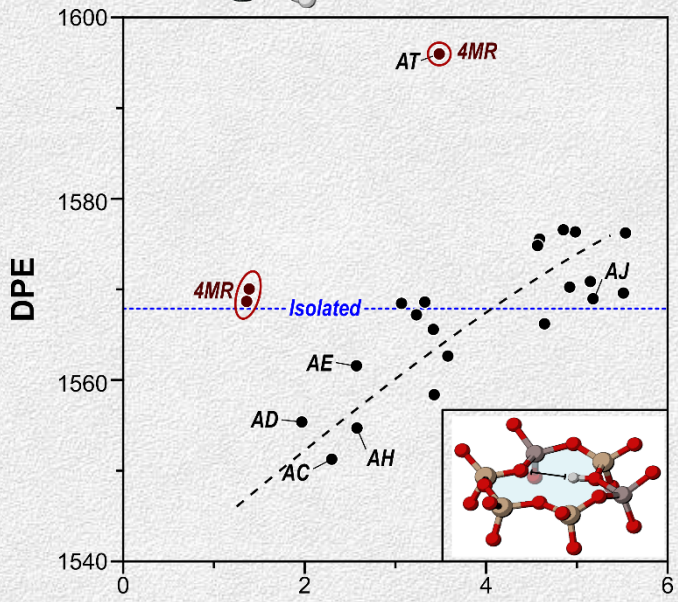
Isolated: 1568

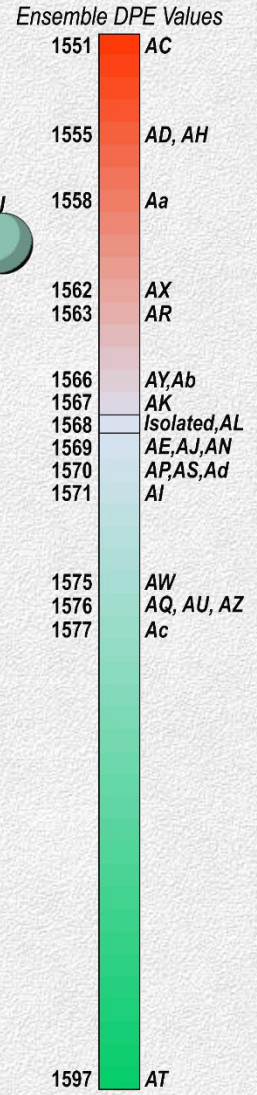
Paired: 1551–1597

DPE		Mono
O1	1569	
O2	1559	
O3	1566	
O4	1567	



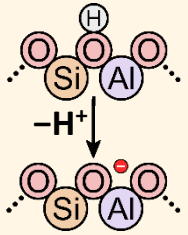






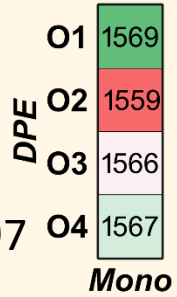
Methanol dehydration in CHA

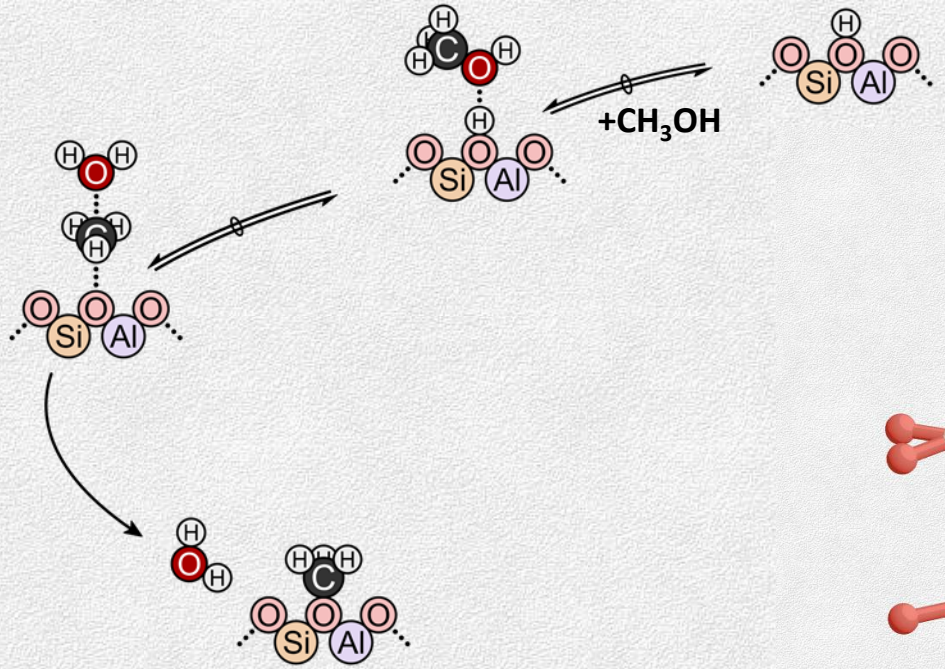
DPE in CHA

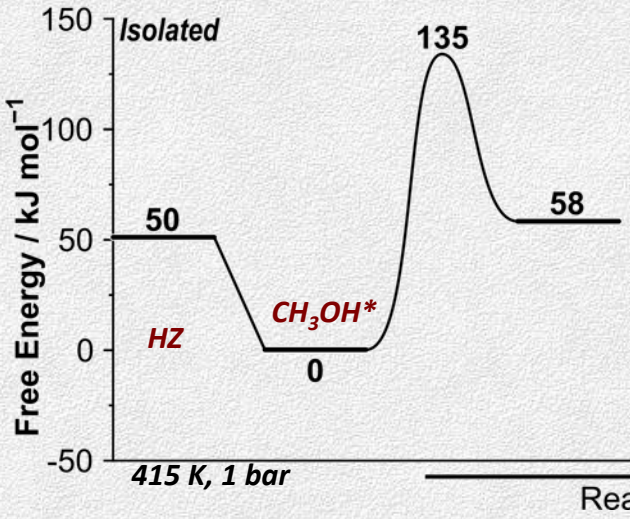


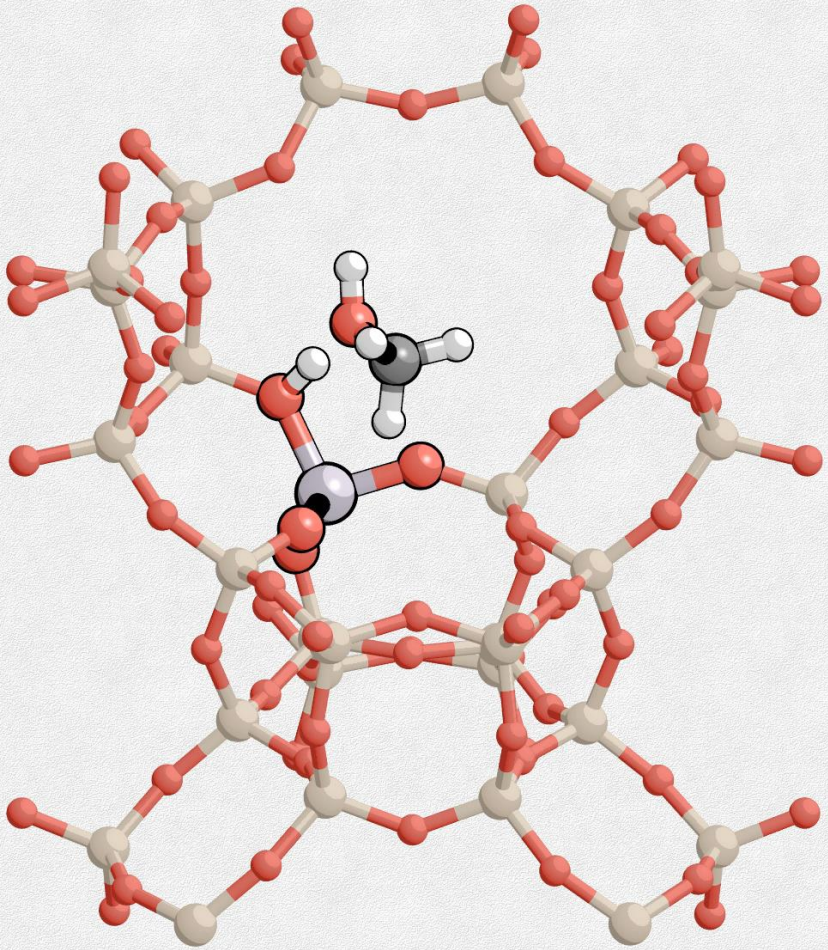
Isolated: 1568

Paired: 1551–1597







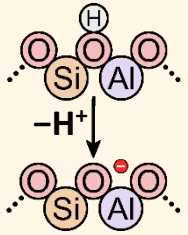


Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

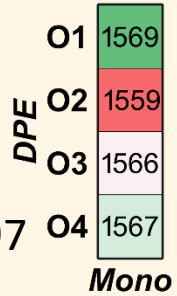
Methanol dehydration in CHA

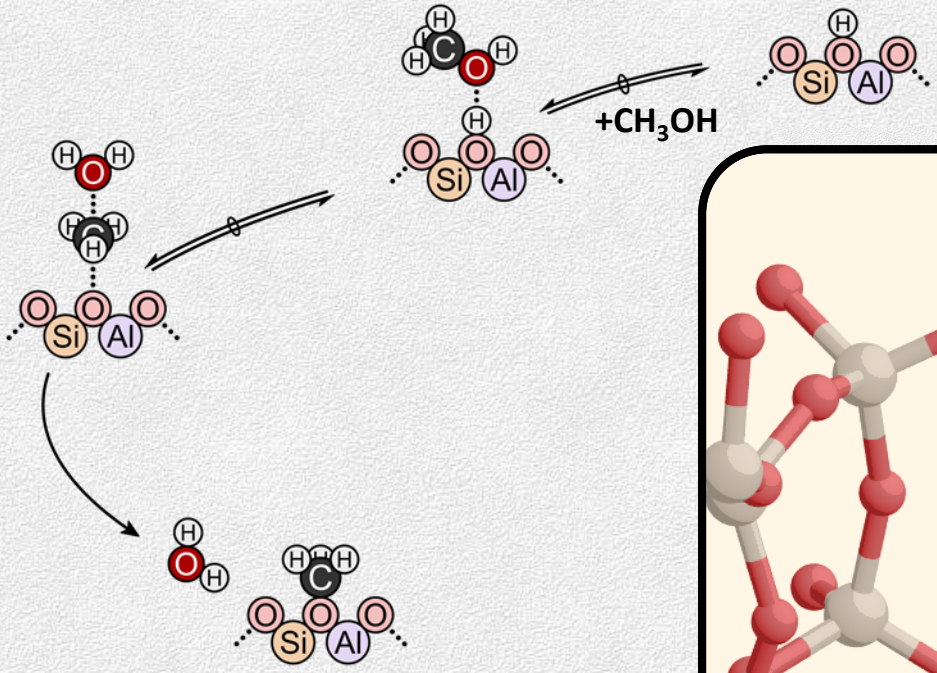
DPE in CHA

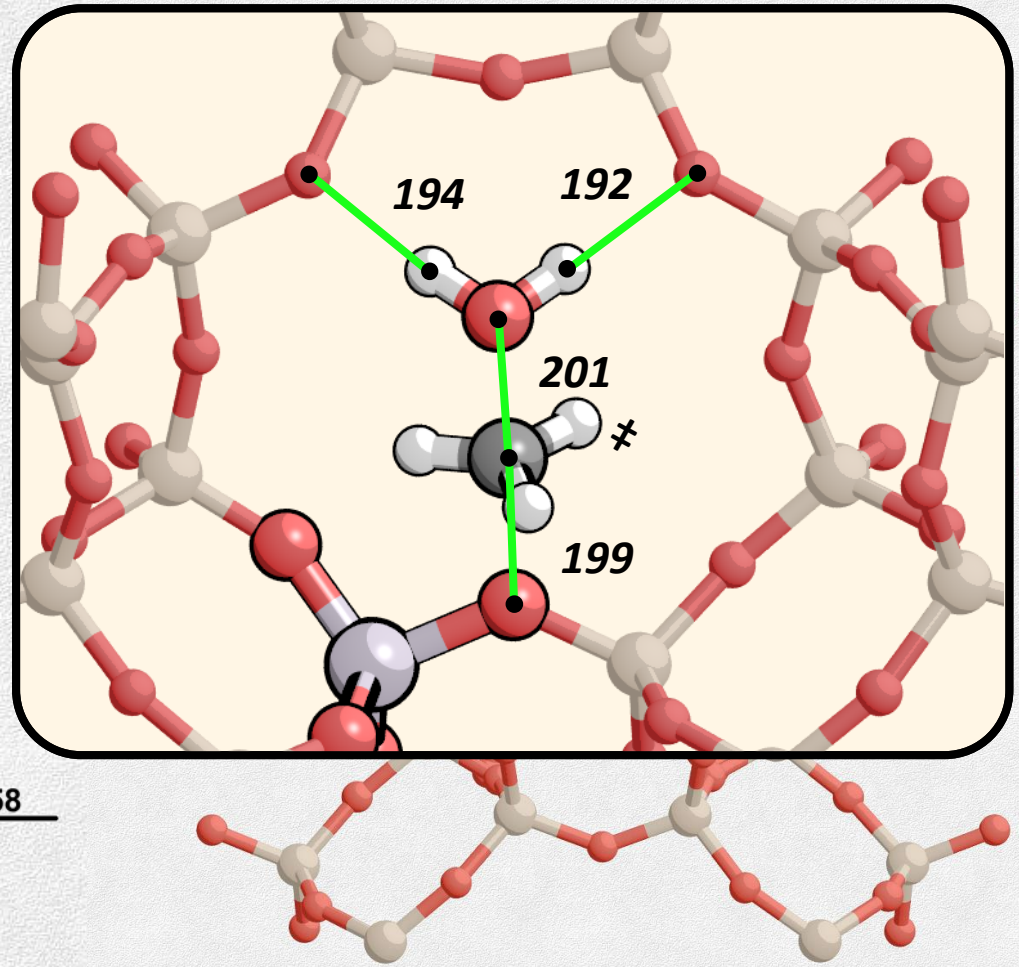


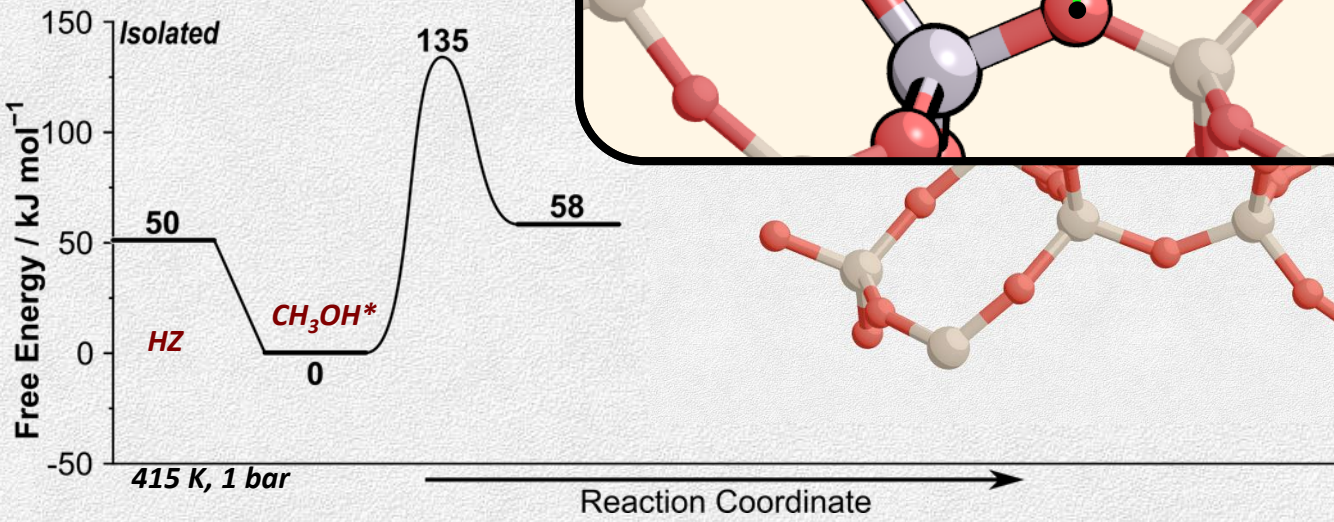
Isolated: 1568

Paired: 1551–1597







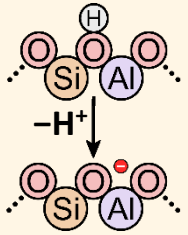


Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

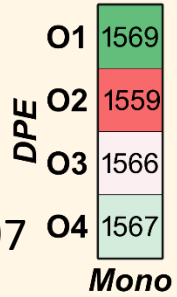
Methanol dehydration in CHA

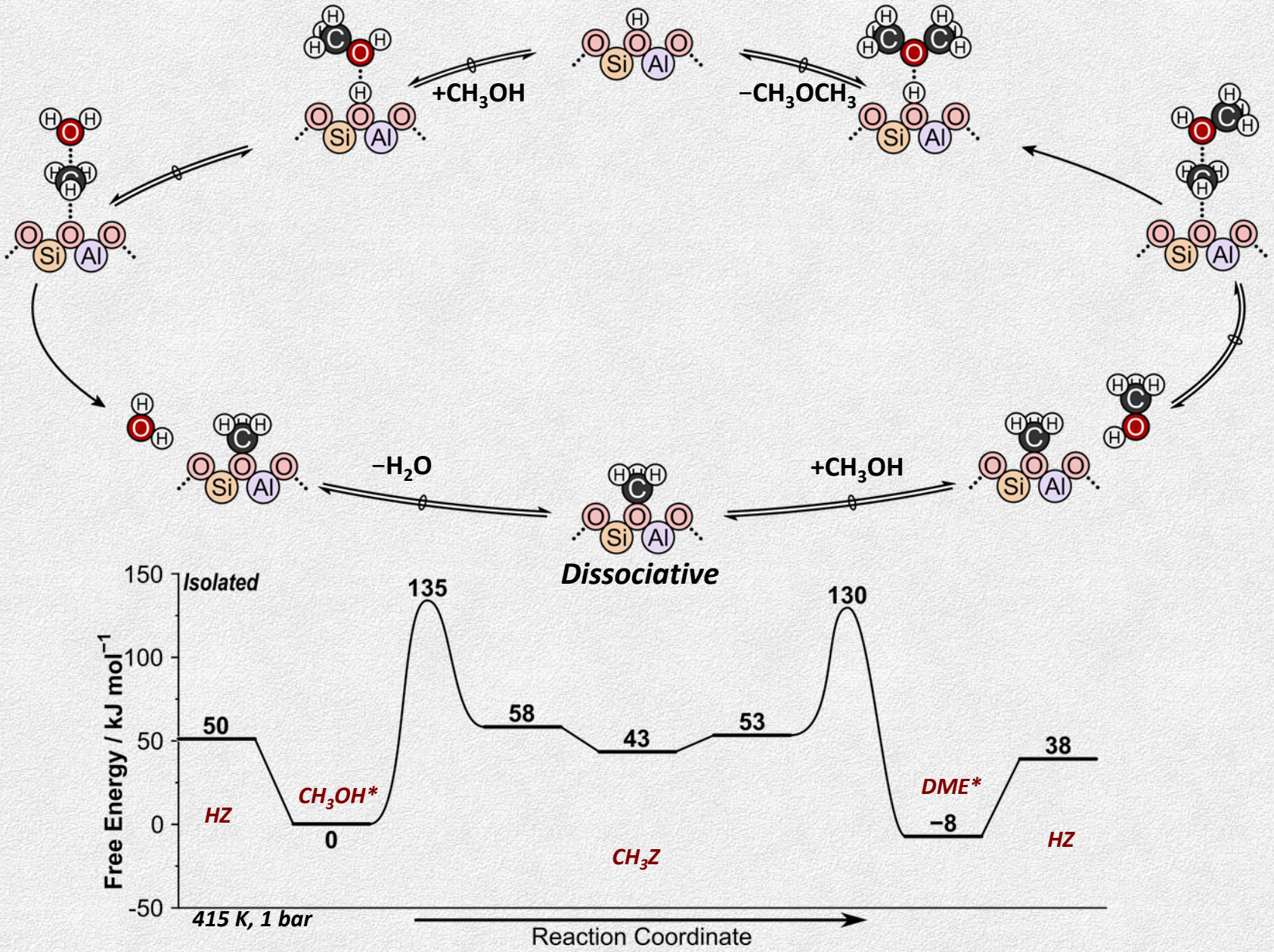
DPE in CHA



Isolated: 1568

Paired: 1551–1597



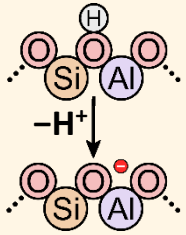


Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

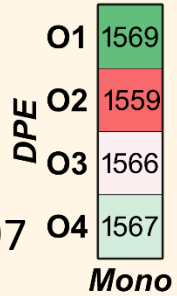
Methanol dehydration in CHA

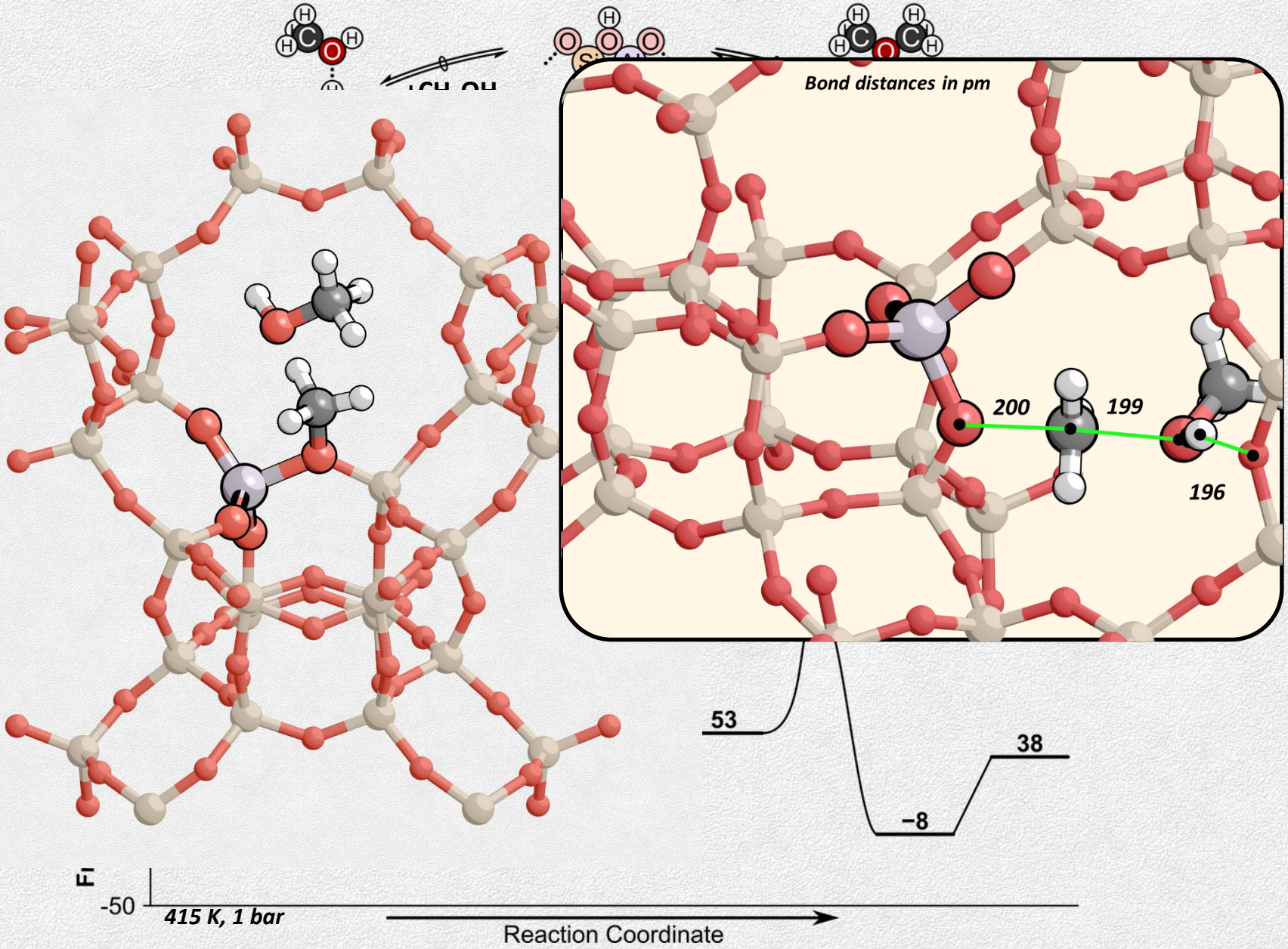
DPE in CHA



Isolated: 1568

Paired: 1551–1597



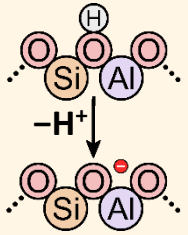


Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

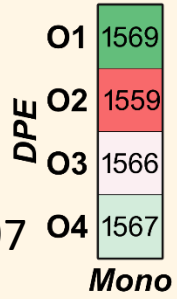
Methanol dehydration in CHA

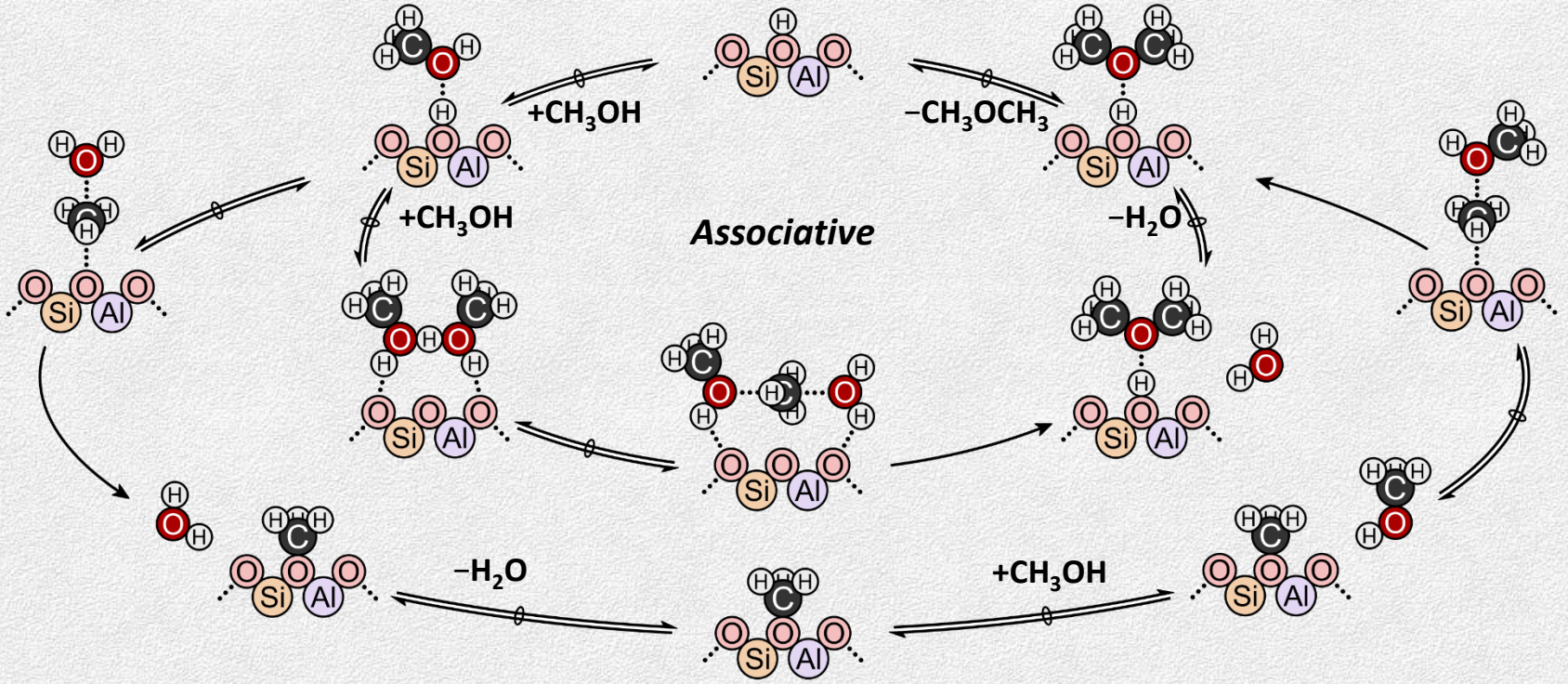
DPE in CHA

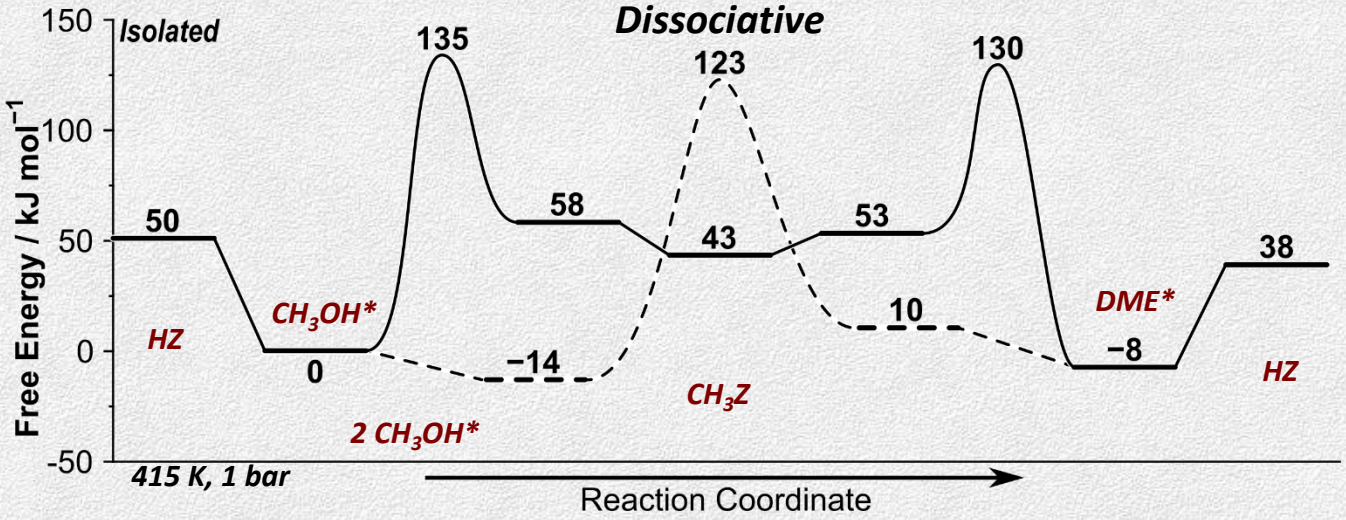


Isolated: 1568

Paired: 1551–1597





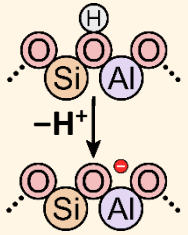


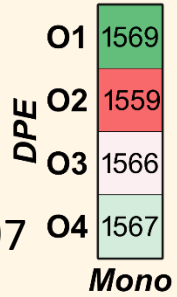
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA



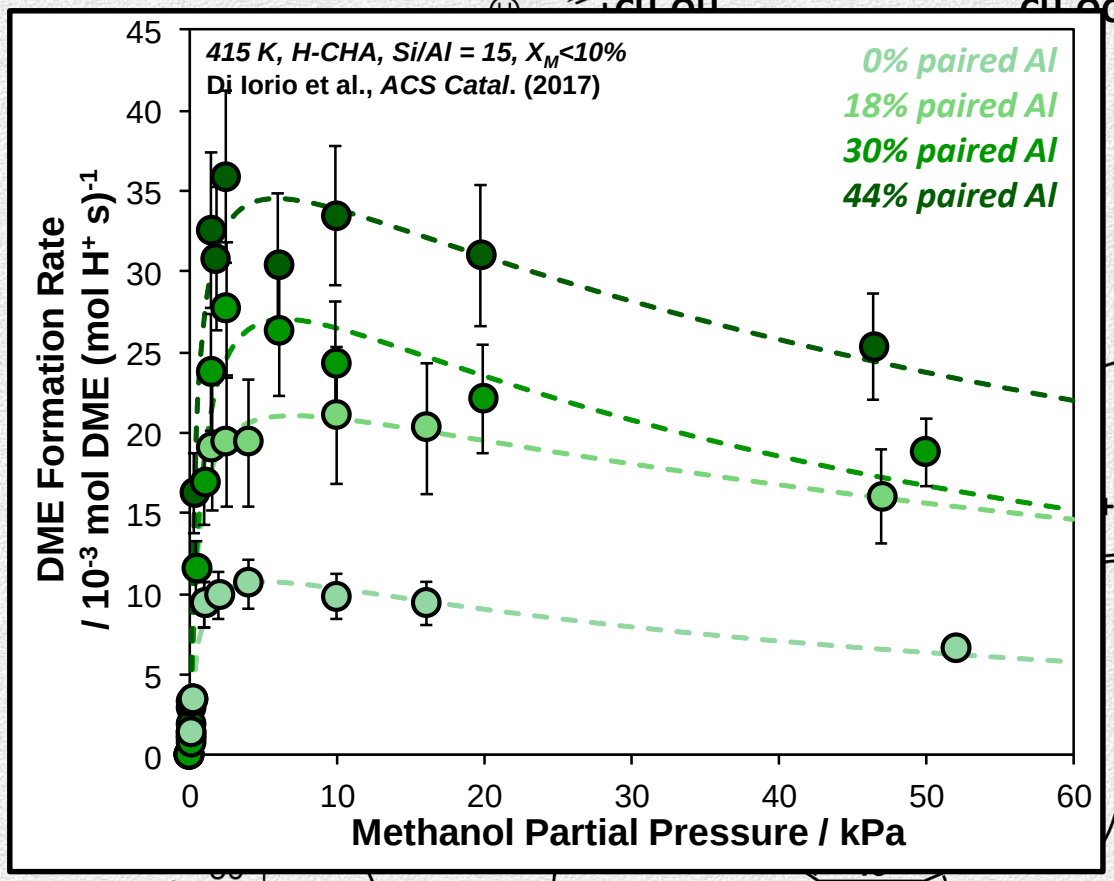


Isolated: 1568

Paired: 1551–1597

Methanol dehydration

Isolated: Associative

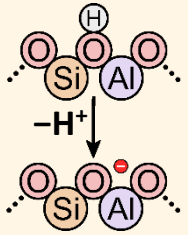


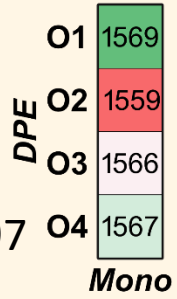
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA



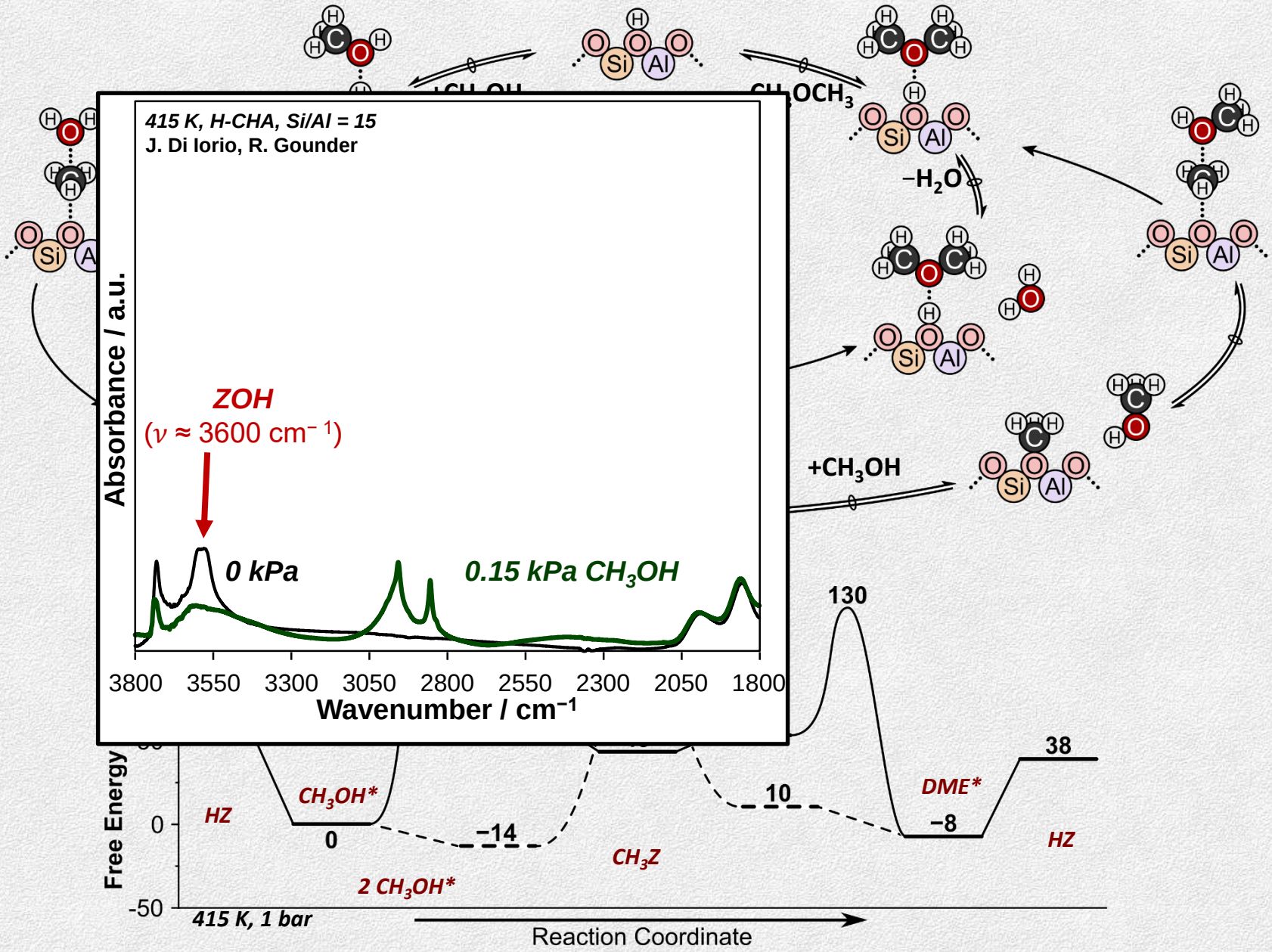


Isolated: 1568

Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol

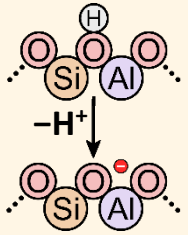


Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

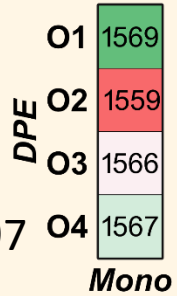
Methanol dehydration in CHA

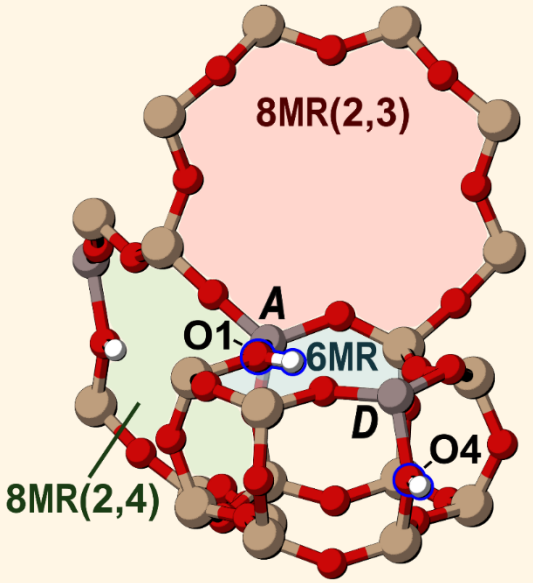
DPE in CHA

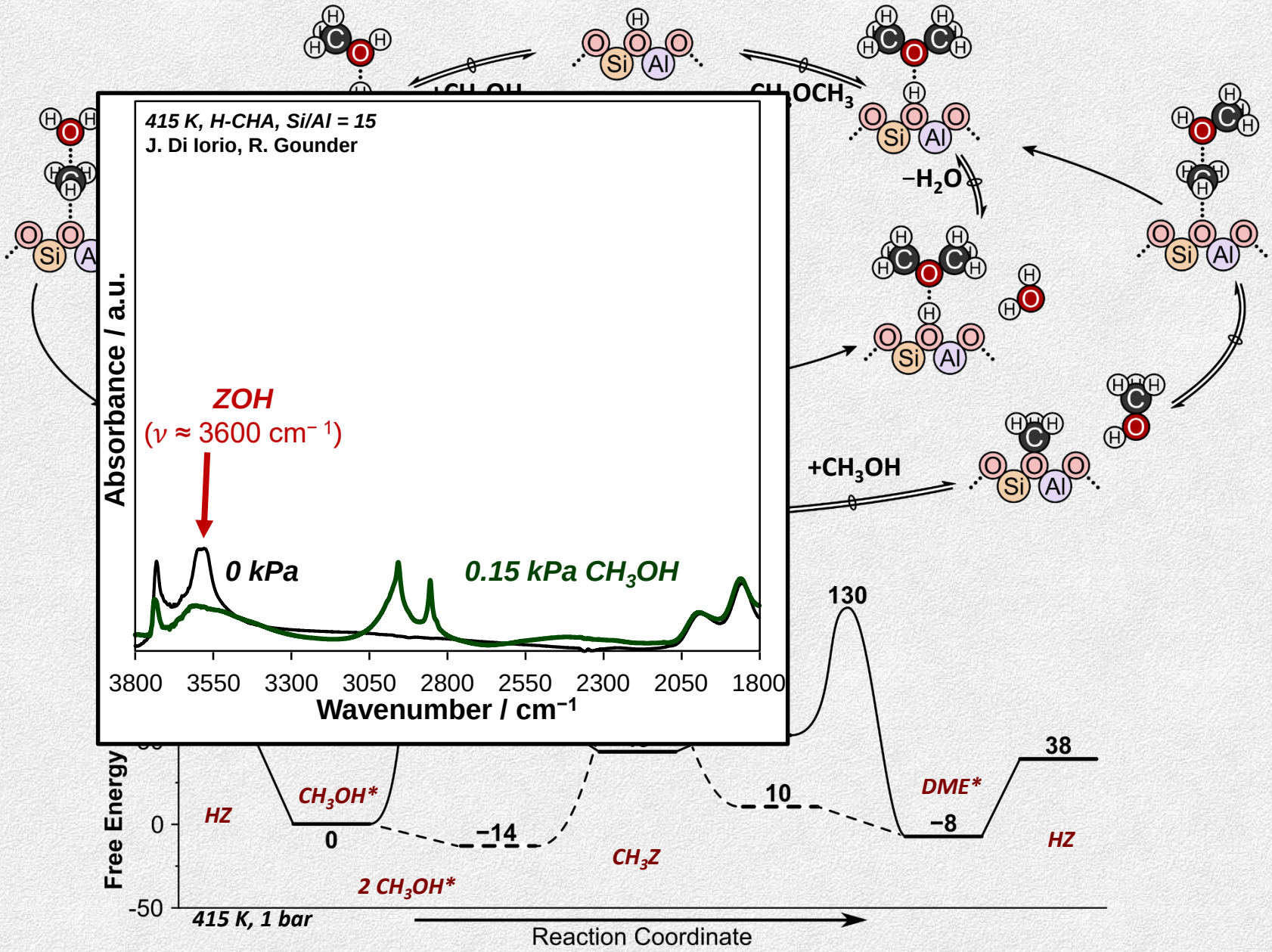


Isolated: 1568

Paired: 1551–1597





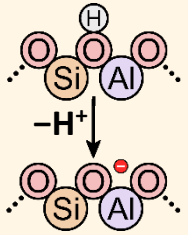


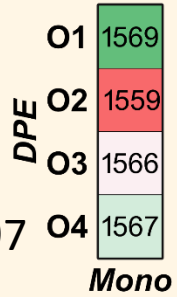
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA



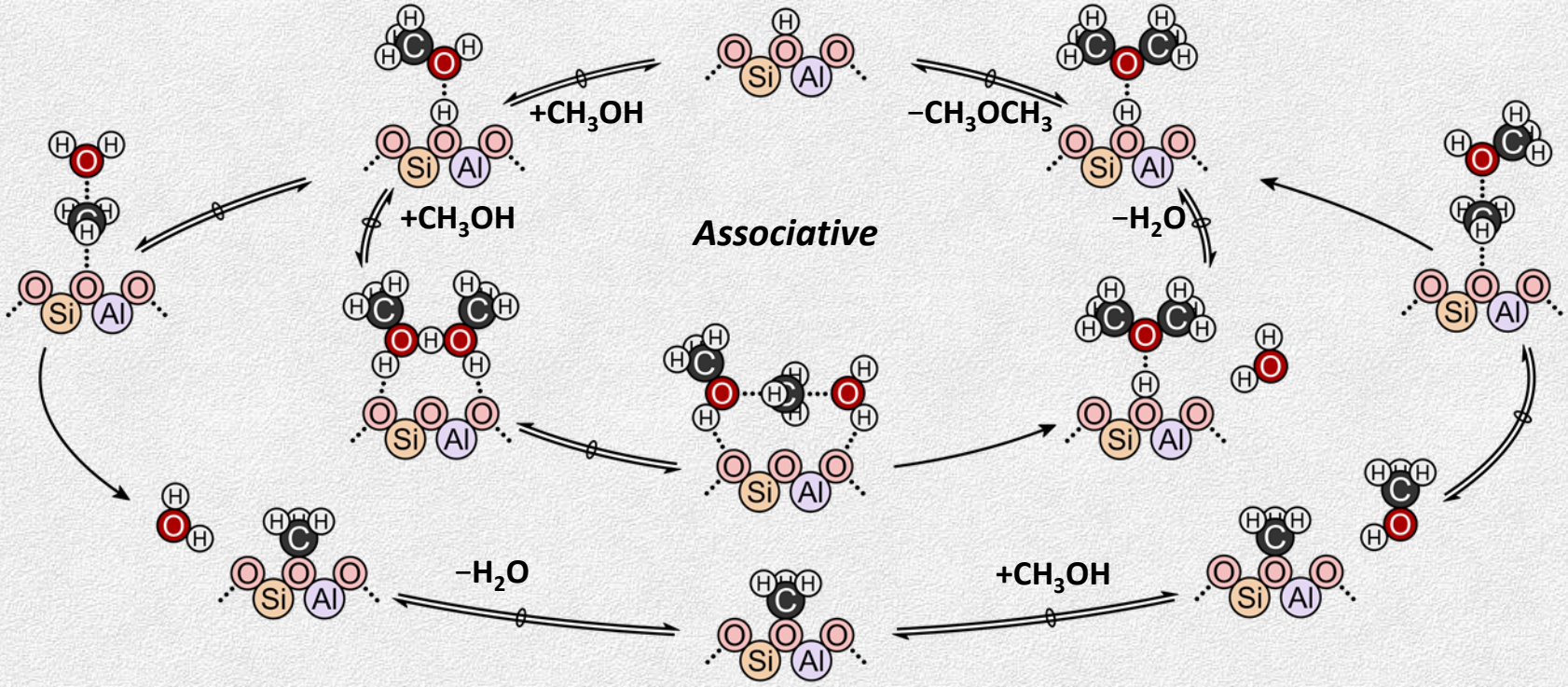


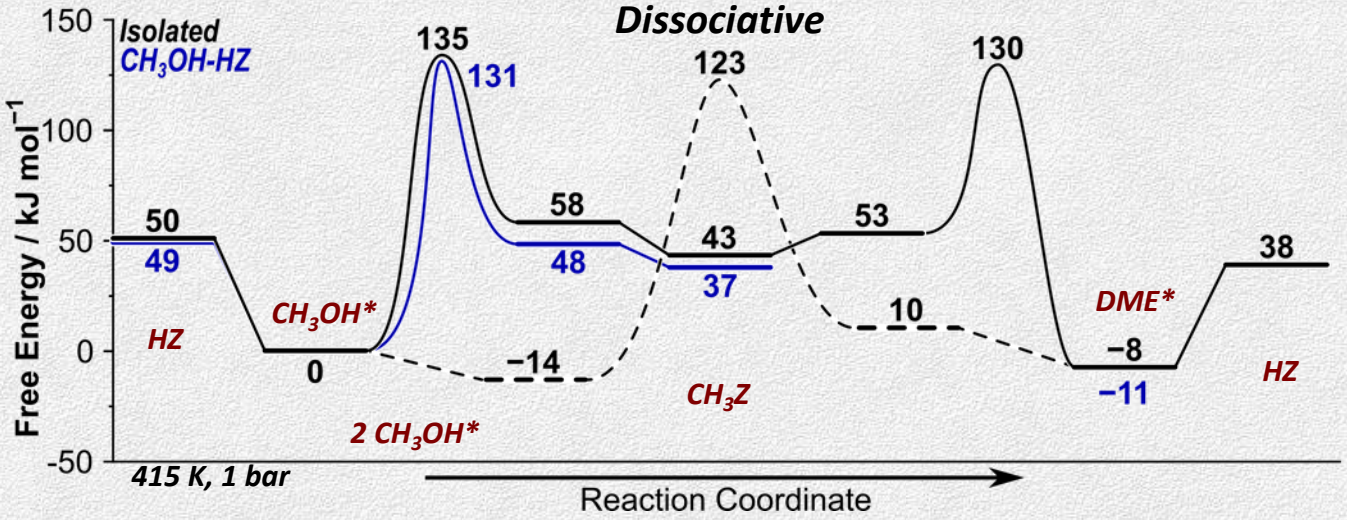
Isolated: 1568

Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol



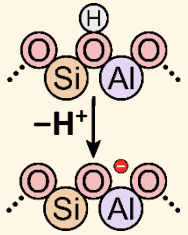


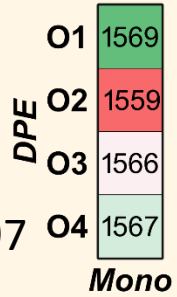
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA



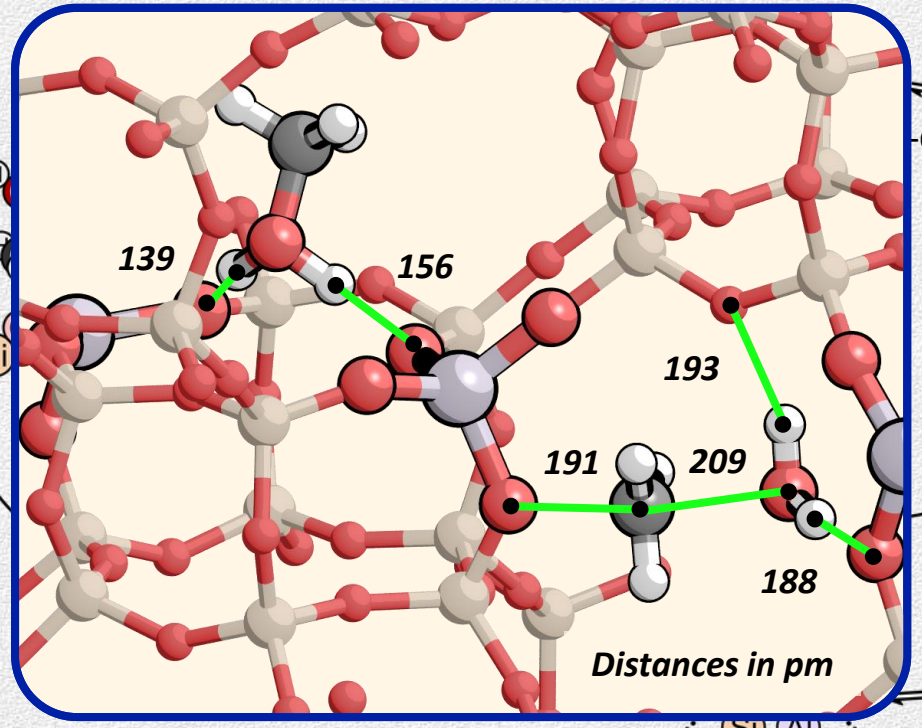


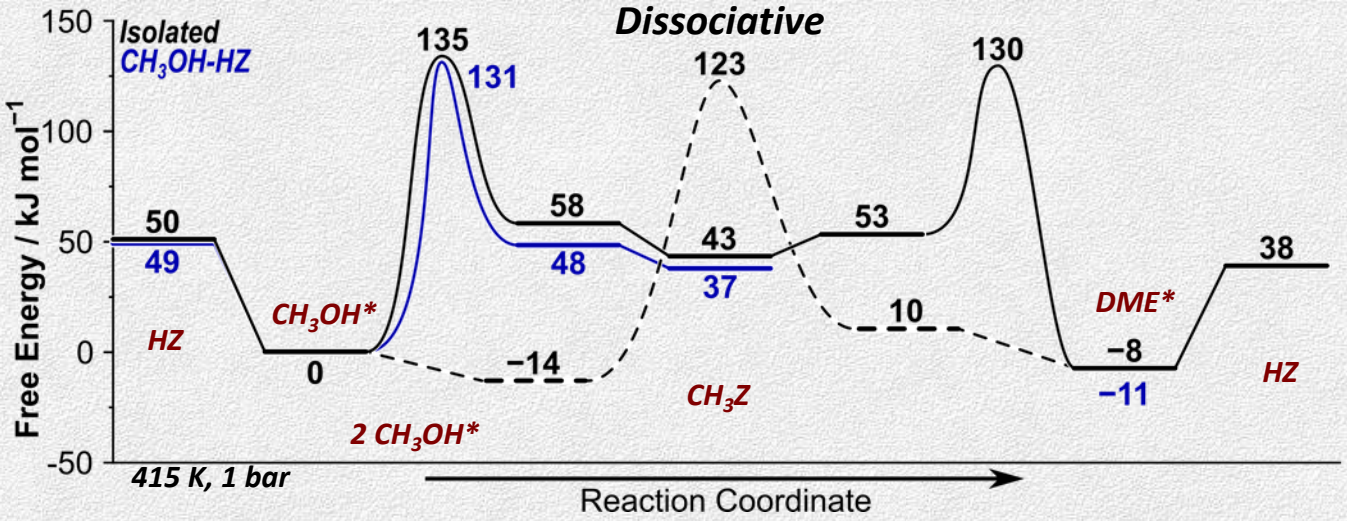
Isolated: 1568

Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol



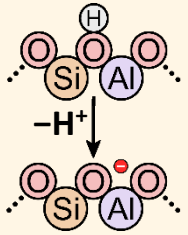


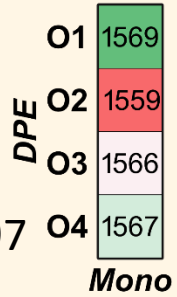
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA



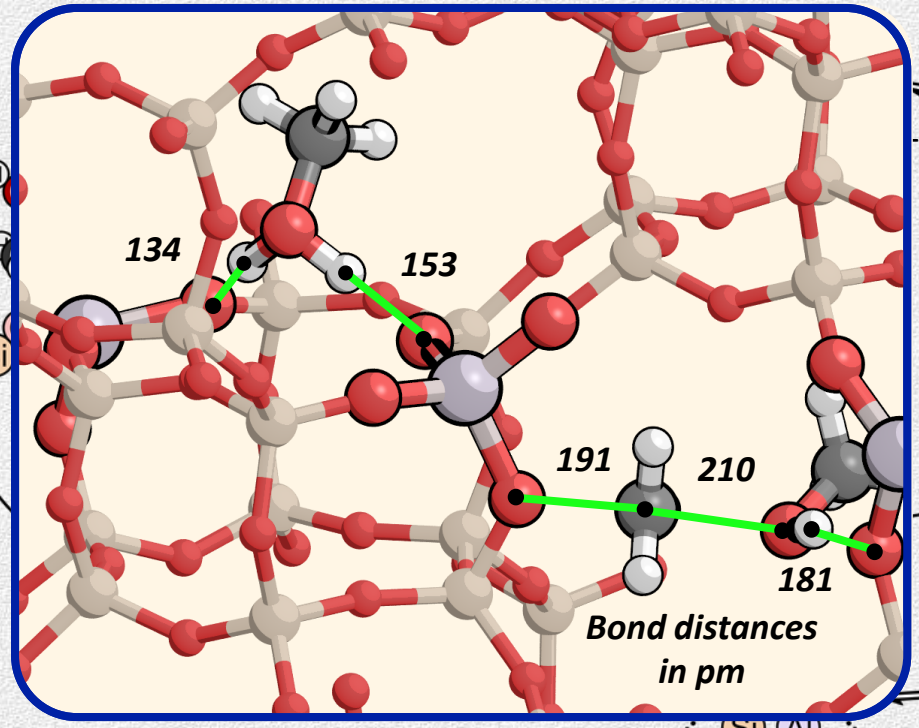


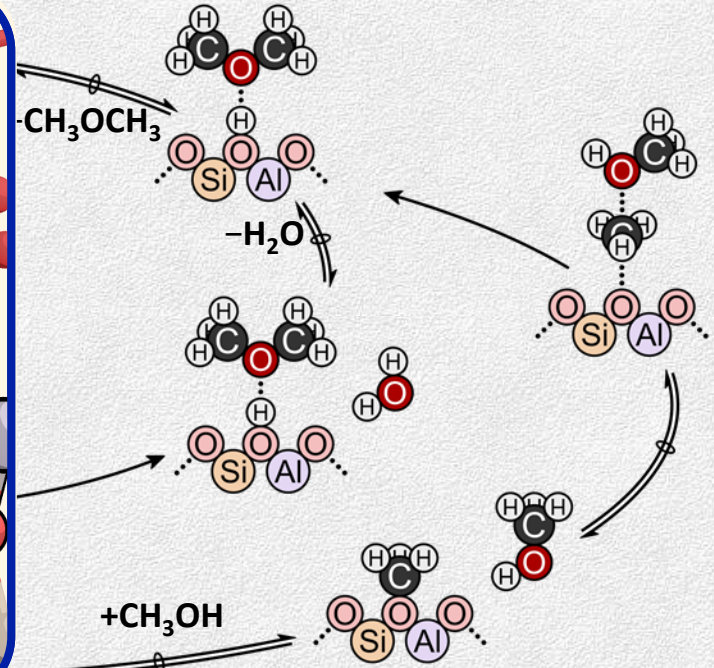
Isolated: 1568

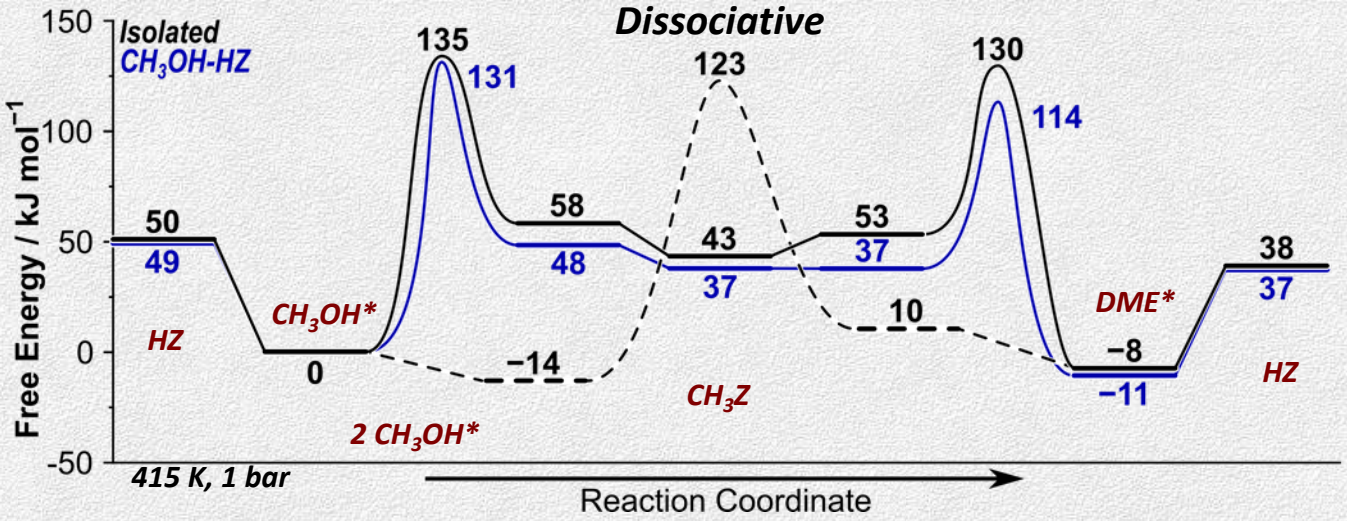
Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol





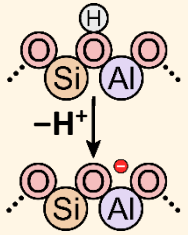


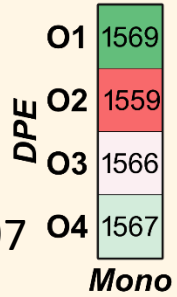
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA



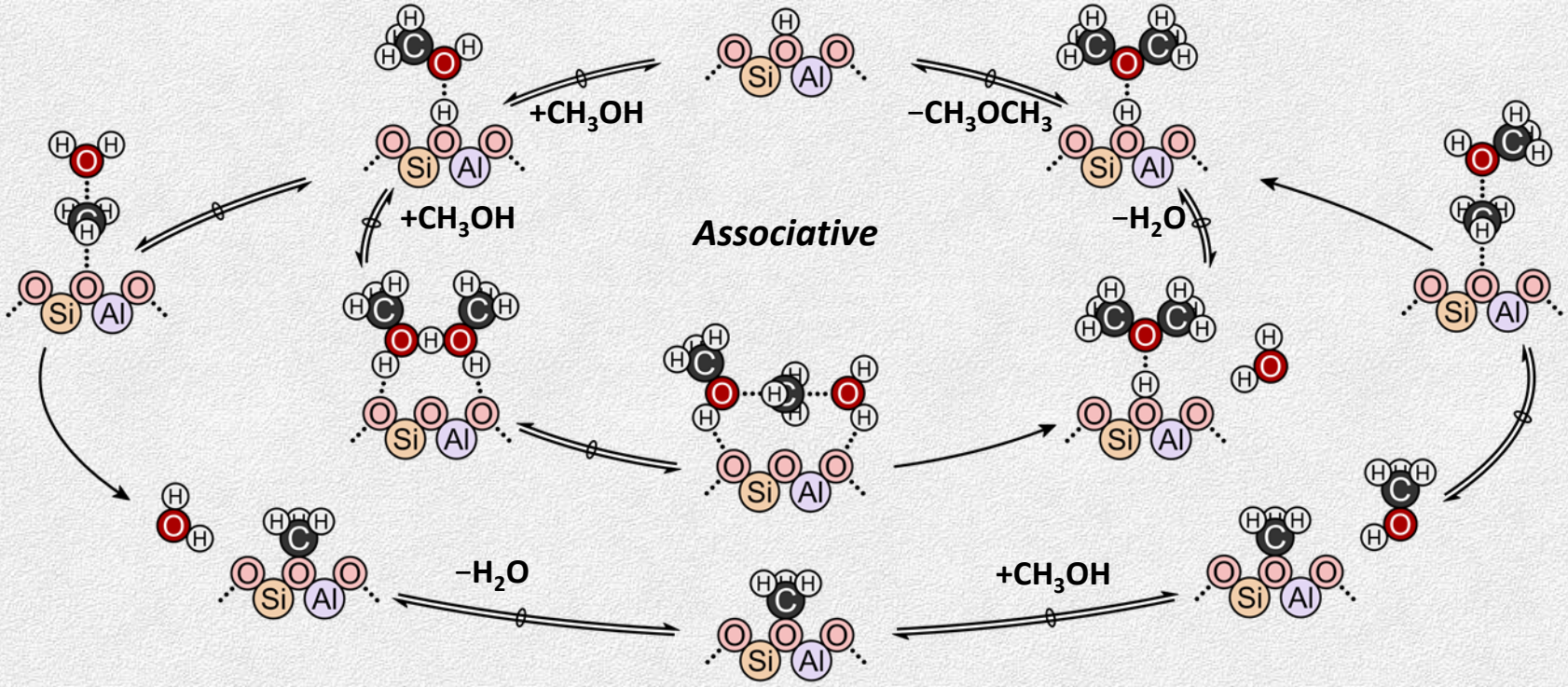


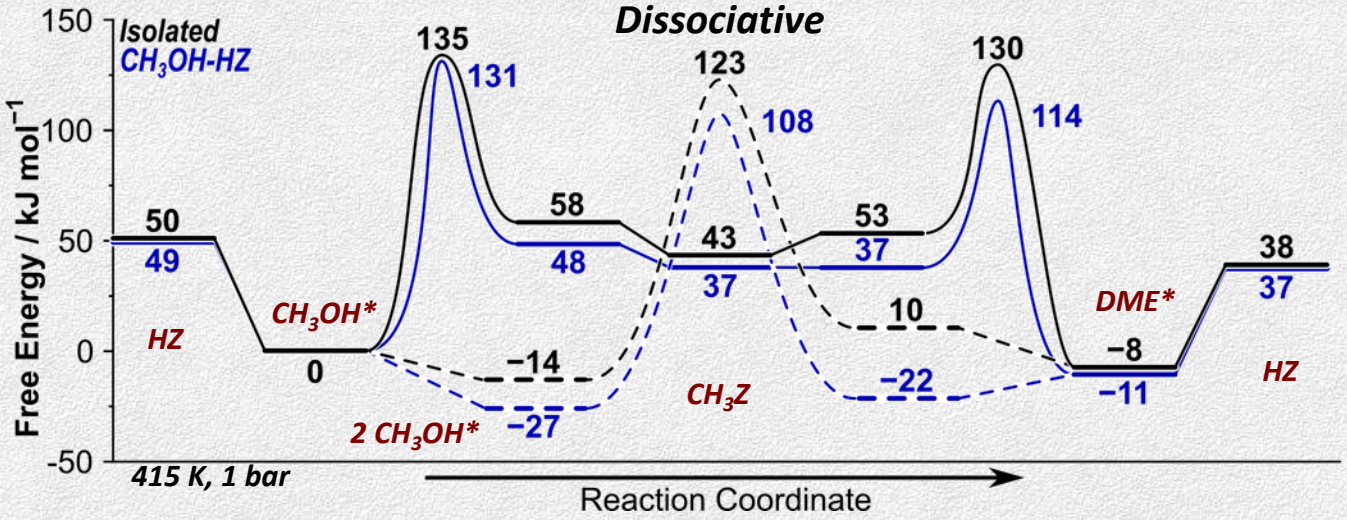
Isolated: 1568

Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol



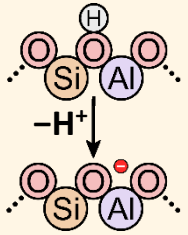


Energies in kJ mol–1

Di Iorio et al., J. Catal (2019)

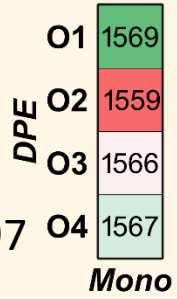
Methanol dehydration in CHA

DPE in CHA



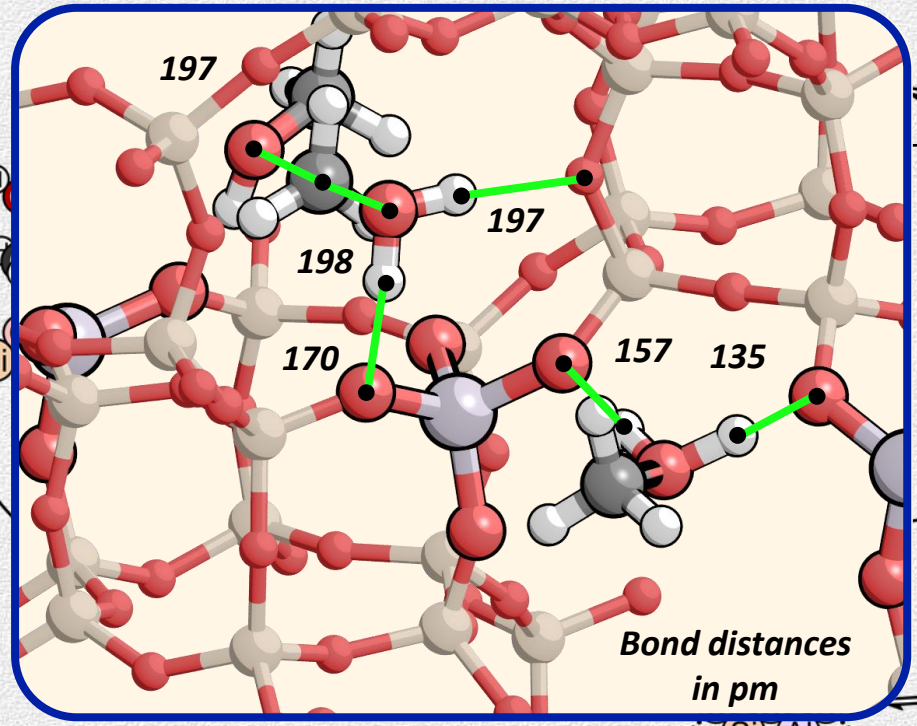
Isolated: 1568

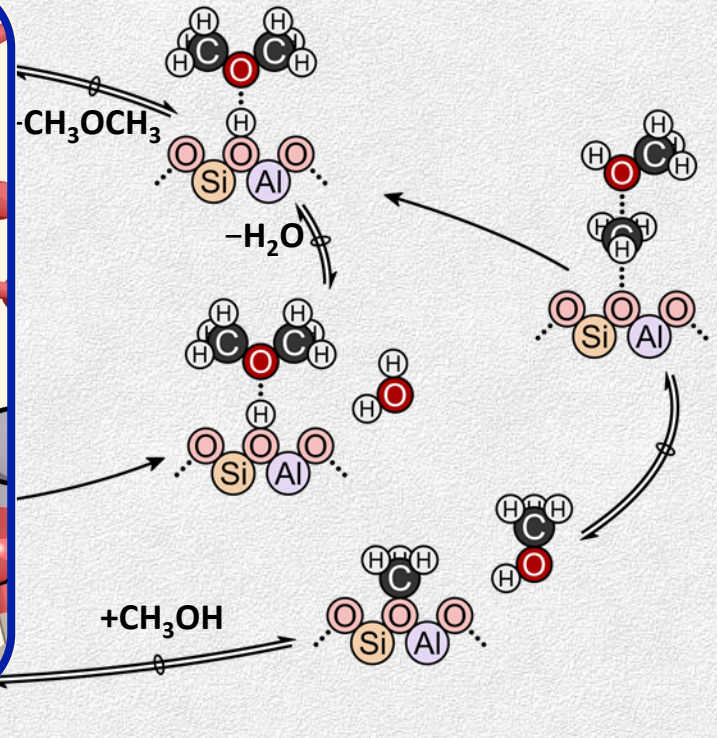
Paired: 1551–1597

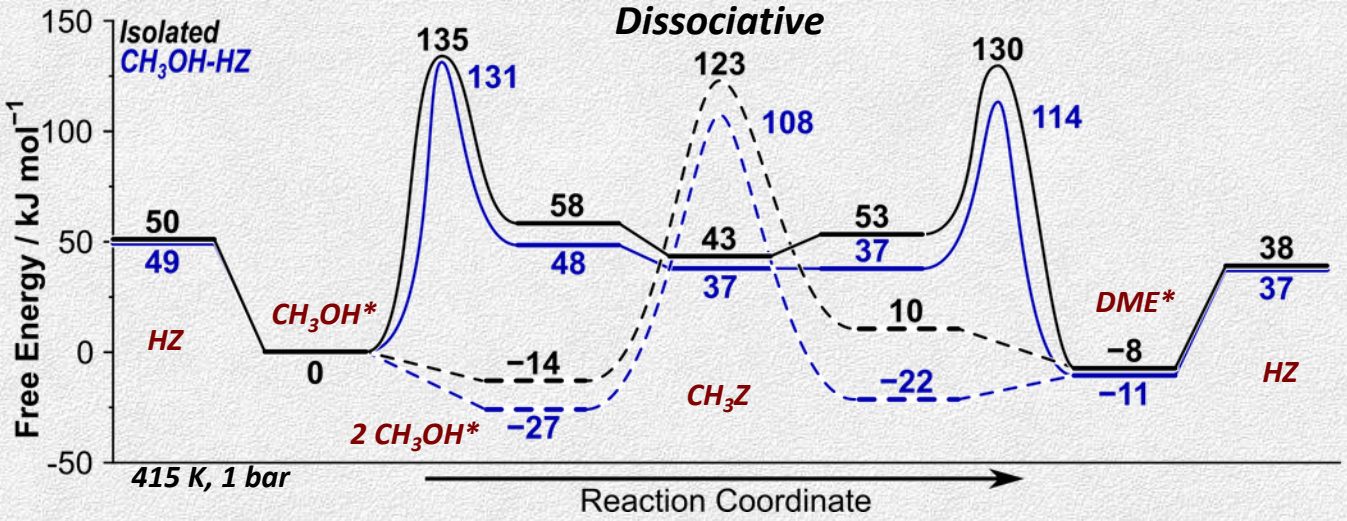


Methanol dehydration

Isolated: Associative
Sites covered in methanol





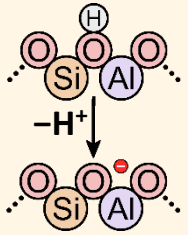


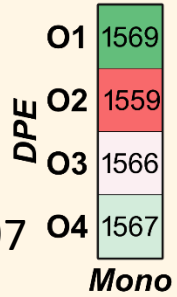
Energies in kJ mol^{-1}

Di Iorio et al., J. Catal (2019)

Methanol dehydration in CHA

DPE in CHA





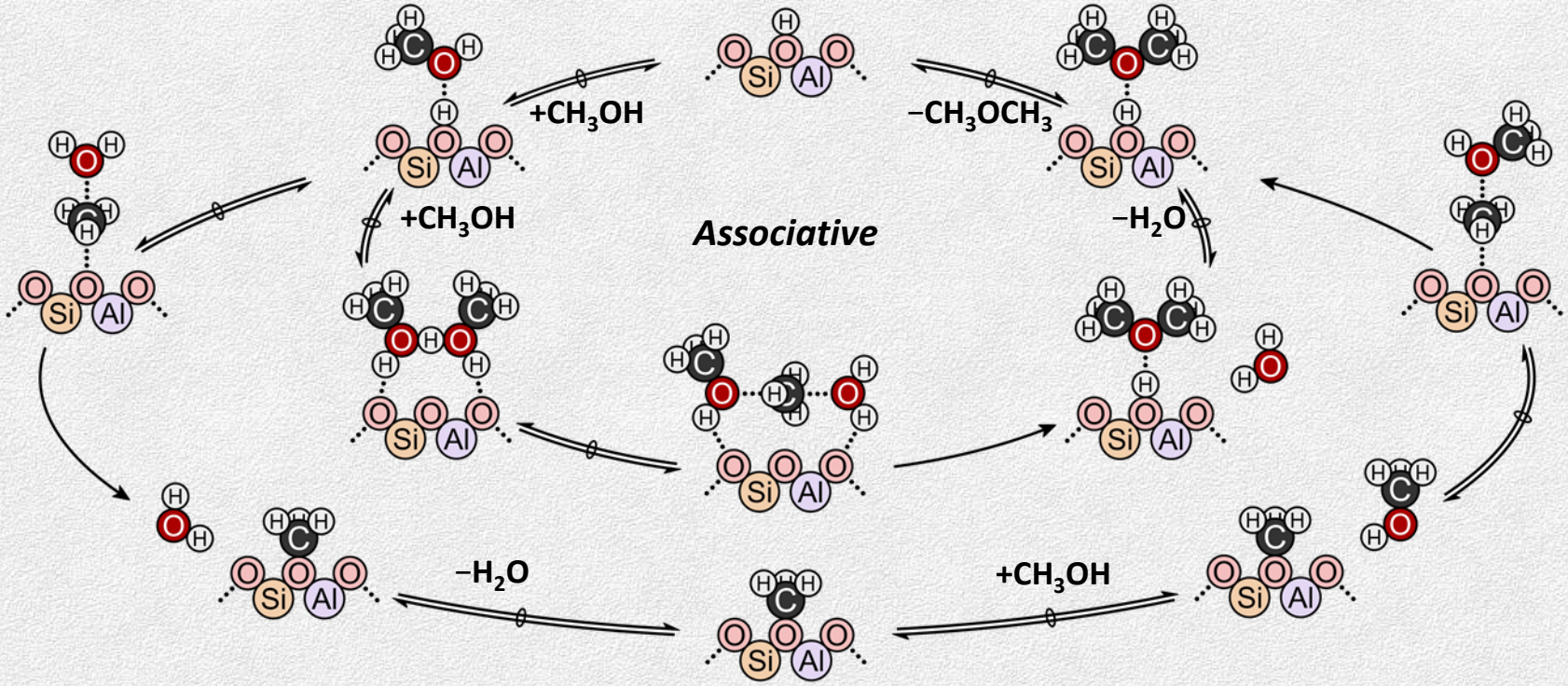
Isolated: 1568

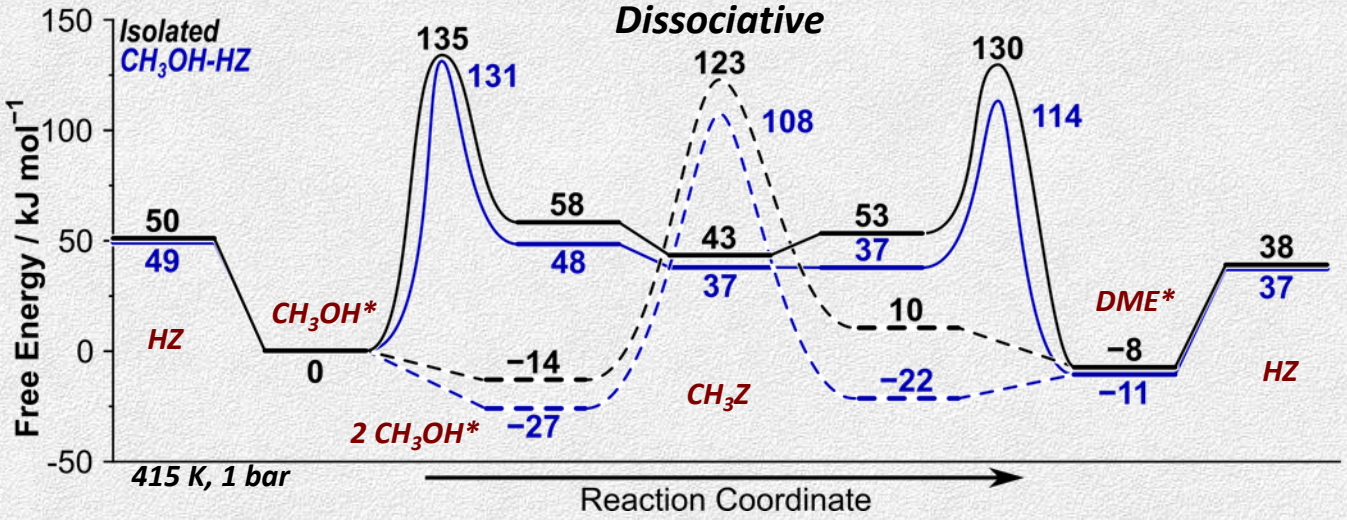
Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol

Paired: Rates increased



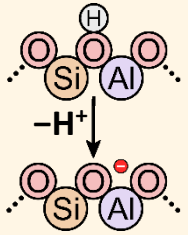


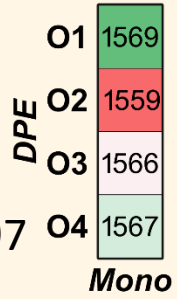
Energies in kJ mol–1

Di Iorio et al., J. Catal (2019)

Recap

DPE in CHA





Isolated: 1568

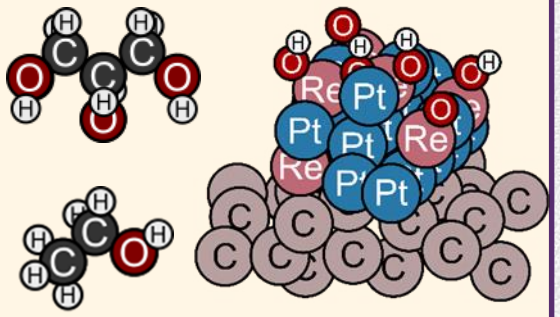
Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol

Paired: Rates increased

Alcohols on metals



Rates $PtReO_x$>$AuReO_x$>Pt

Rates ethanol > glycerol

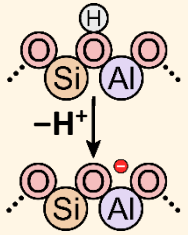
ReO_x
Promotes 1°C–O cleavage
Facilitates 2°C–O cleavage
Reduces C–C cleavage

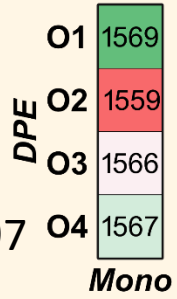
$AuReO_x$ produces
unsaturated compounds

Energies in kJ mol^{-1}

Recap

DPE in CHA





Isolated: 1568

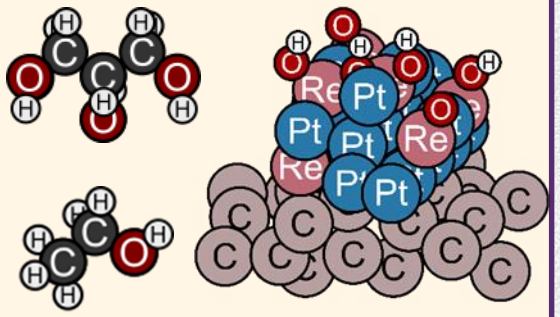
Paired: 1551–1597

Methanol dehydration

Isolated: Associative
Sites covered in methanol

Paired: Rates increased
Mechanism shift?

Alcohols on metals



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Rates ethanol > glycerol

ReO_x
Promotes 1°C–O cleavage
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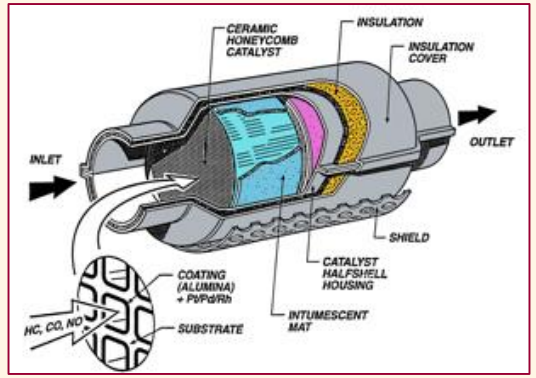
Reduces C–C cleavage

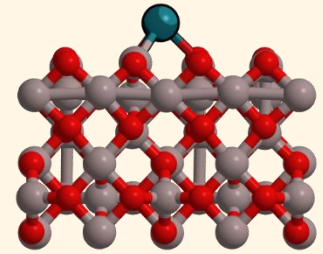
$AuReO_x$ produces
unsaturated compounds

Emission control
(3-way catalytic
converter)



Metals:
Pt, Pd, Rh

Suffer at start up (low T.)



Atomic Rh

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Energies in kJ mol^{-1}

NO_x reduction and CO oxidation

Rh particles

CO oxidation

NO_x reduction

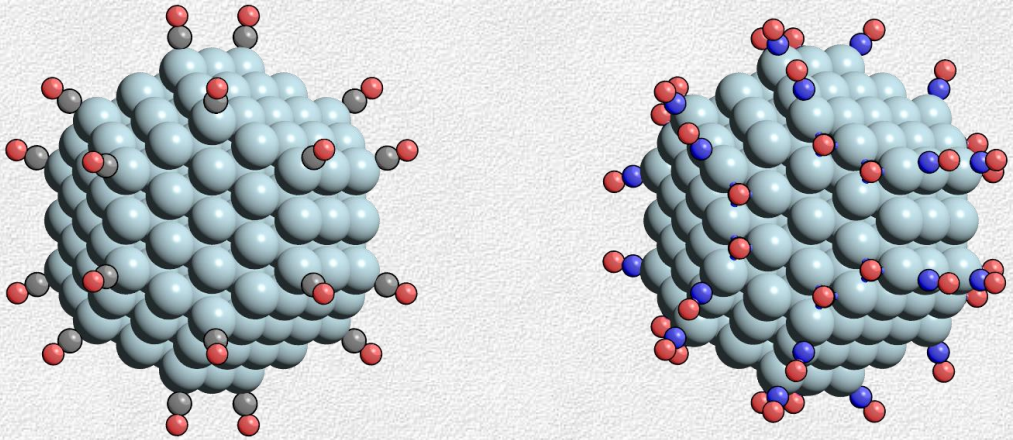
Binding energies

Why Rh?
↑rates & selectivity to N2

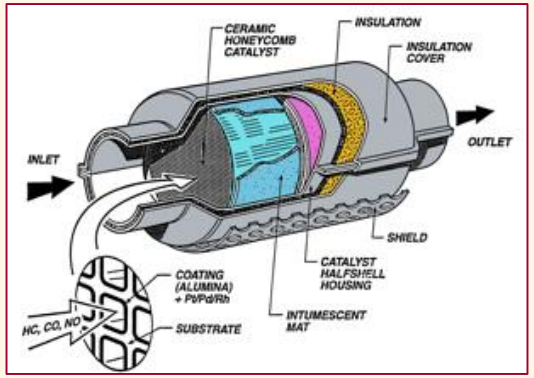
↓ volatility

$CO, C_xH_y, NO_x \rightarrow CO_2, N_2, H_2O$

Standard Operating Temp
900–1100 K

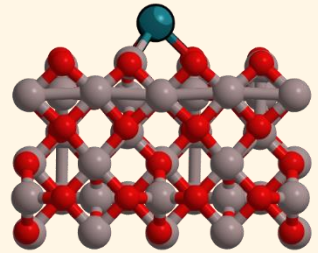


Emission control
(3-way catalytic
converter)



Metals:
Pt, Pd, Rh

Suffer at start up (low T.)



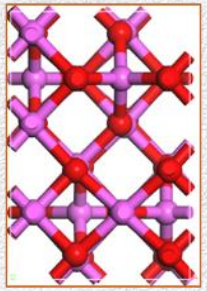
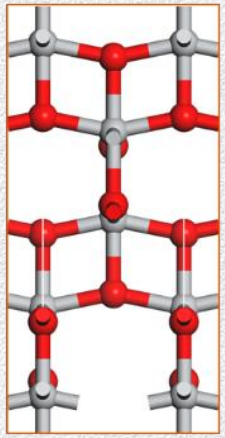
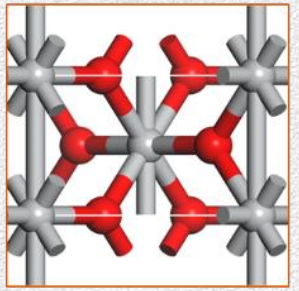
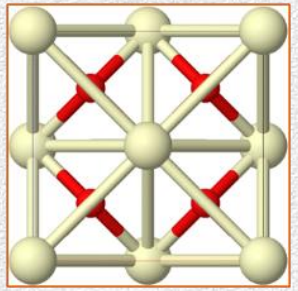
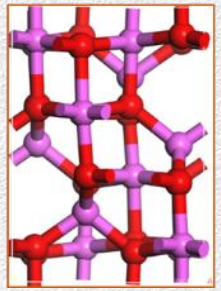
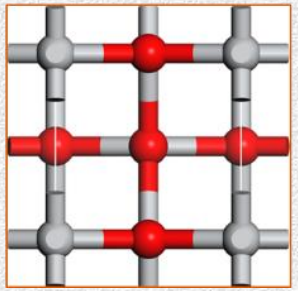
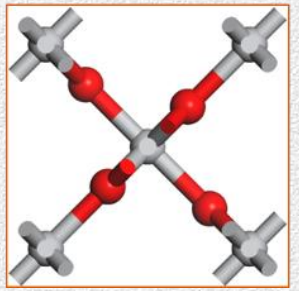
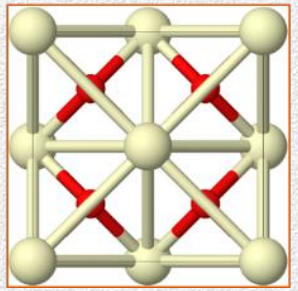
Atomic Rh

Catalytic converter image: meca.org

Bulk structures

Oxides studied:
(DFT)

- γ-Al_2O_3
- TiO_2-Anatase
- TiO_2-Rutile
- CeO_2

	γ-Al_2O_3	TiO_2-Anatase	TiO_2-Rutile	CeO_2
Top View				
Side View				

Bulk structures

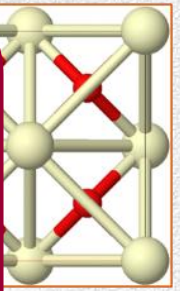
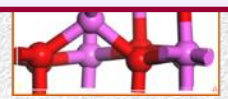
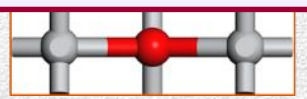
Oxides studied:
(DFT)

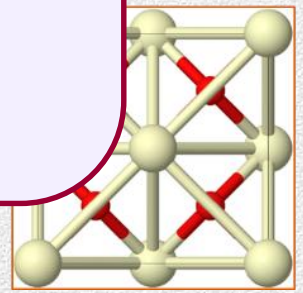
- γ-Al_2O_3
- TiO_2-Anatase
- TiO_2-Rutile
- CeO_2

γ-Al_2O_3 | TiO_2-Anatase | TiO_2-Rutile | CeO_2

Top Vi

Side Vie



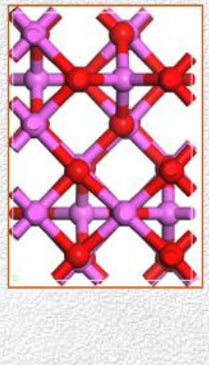
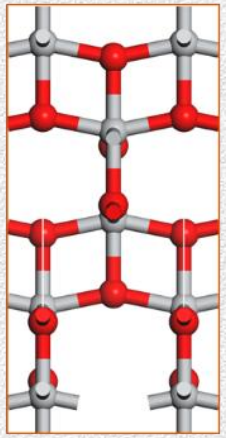
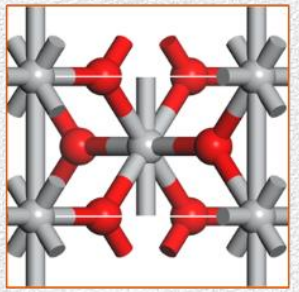
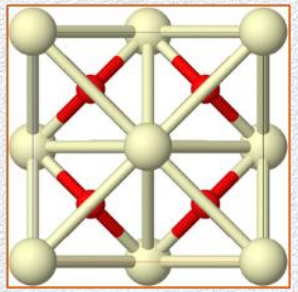
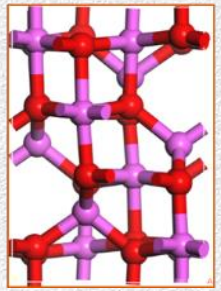
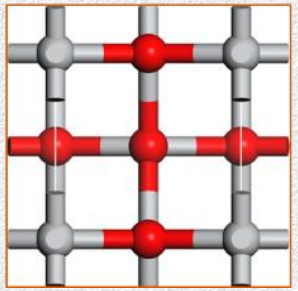
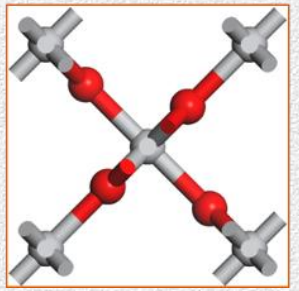
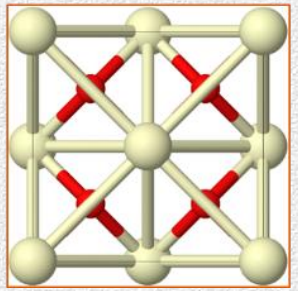
$$Surface\ formation\ energy = \frac{(E_s - N_s * \frac{E_b}{N_b})}{2A}$$

E_s = Energy surface
E_b = Energy bulk
N_s = Number of atoms in surface
N_b = Number of atoms in bulk
A = Surface area

Bulk structures

Oxides studied:
(DFT)

- γ-Al_2O_3
- TiO_2-Anatase
- TiO_2-Rutile
- CeO_2

	γ-Al_2O_3	TiO_2-Anatase	TiO_2-Rutile	CeO_2
Top View				
Side View				

	γ-Al_2O_3				TiO_2 Anatase					TiO_2 Rutile	CeO_2	
Facet/Term.	100	001	010	111	100	001	110	101	111	110	110	111
A	16.8	22.2	19.5	20.3	6.0	18.9	9.5	9.0	28.0	5.7	6.5	2.9
B	14.9	17.2	18.1			5.8						
C	12.5		11.7									

Energies in kJ mol^{-1} Å^{-1}

Bulk structures

Oxides studied:
(DFT)

- γ-Al_2O_3
- TiO_2-Anatase
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	γ-Al_2O_3				TiO_2 Anatase					TiO_2 Rutile	CeO_2	
Facet/Term.	100	001	010	111	100	001	110	101	111	110	110	111
A	16.8	22.2	19.5	20.3	6.0	18.9	9.5	9.0	28.0	5.7	6.5	2.9
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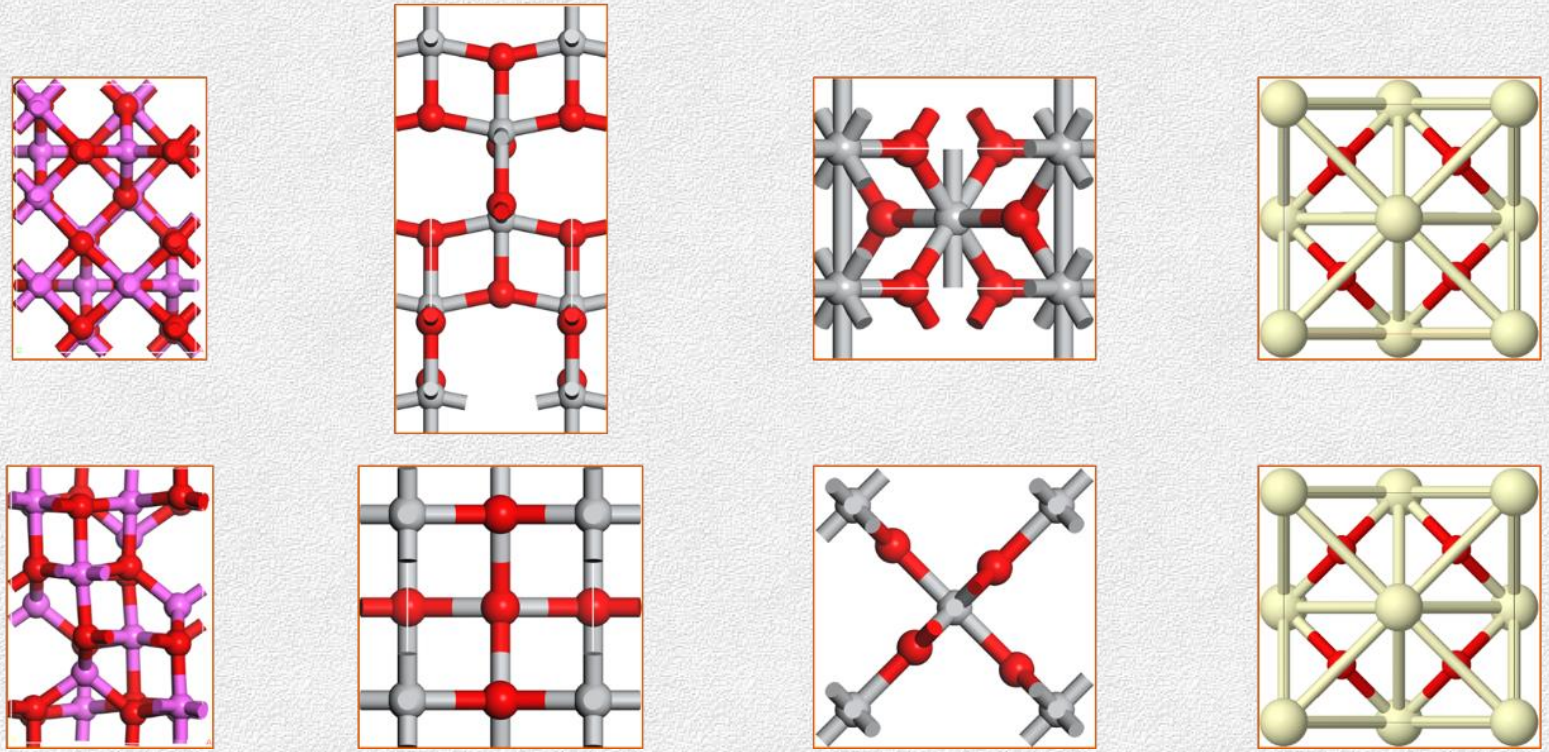

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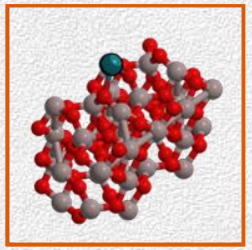
Energies in kJ mol^{-1} Å^{-1}

CO on γ-Al_2O_3 (010)

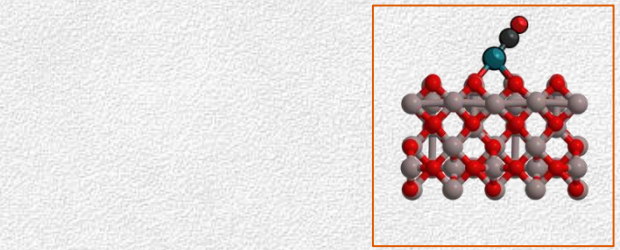
Oxides studied:
(DFT)

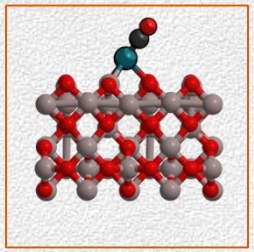
γ-Al_2O_3 (010)

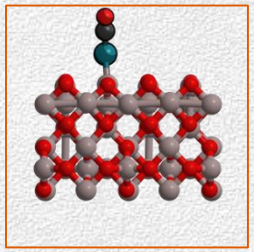
Rh	3-fold
1st CO BE (G)	−266



(Rel. E_0) *(0)*







(Rel. E_0)		*(0)*		*(3)*		*(28)*	
Mobile B.E.	1st CO BE	***−253***	***−266***	***−250***	***−263***	***−226***	***−240***
		H	*G*				

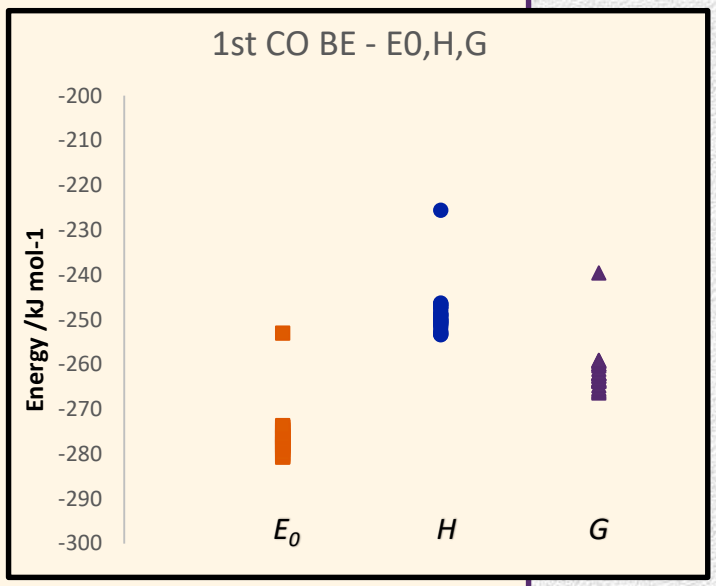
Energies in kJ mol^{-1}, 573 K, 1 bar

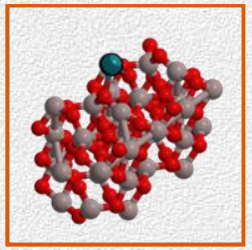
CO on γ-Al_2O_3 (010)

Oxides studied:
(DFT)

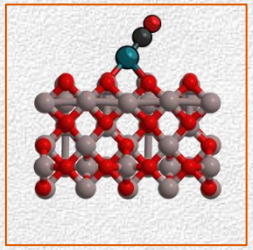
γ-Al_2O_3 (010)

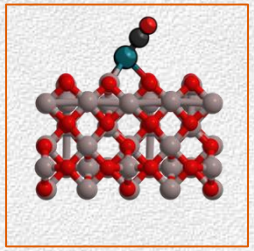
Rh	3-fold
1st CO BE (G)	−266

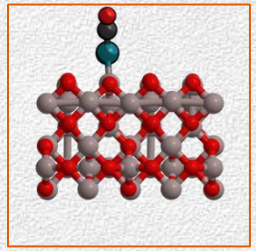




(Rel. E_0) *(0)*







(Rel. E_0)		*(0)*		*(3)*		*(28)*	
Mobile B.E.	1st CO BE	*−253*	*−266*	*−250*	*−263*	*−226*	*−240*
		H	*G*				

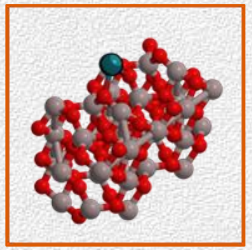
Energies in kJ mol^{-1}, 573 K, 1 bar

2CO on γ-Al_2O_3 (010)

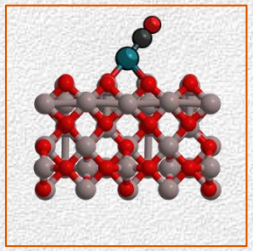
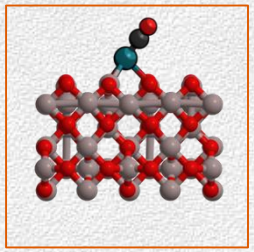
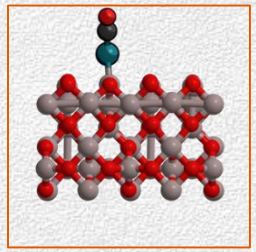
Oxides studied:
(DFT)

γ-Al_2O_3 (010)

Rh	3-fold
1st CO BE (G)	−266
2nd CO BE (G)	−114



(Rel. E_0) *(0)*

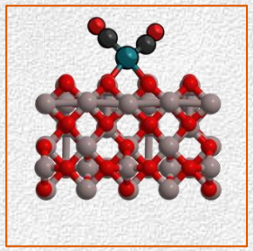
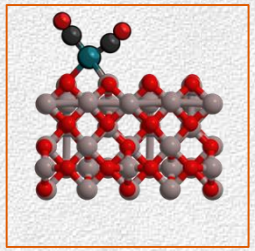
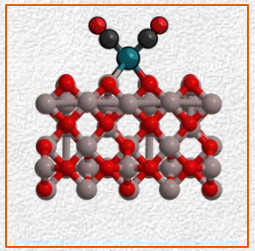
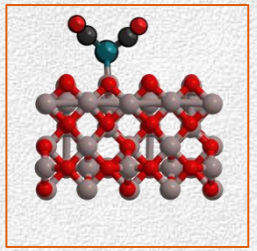
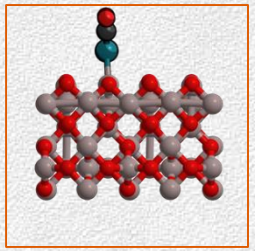




(Rel. E_0) *(0)* *(3)* *(28)*

Mobile B.E. 1st CO BE ***−253*** ***−266*** ***−250*** ***−263*** ***−226*** ***−240***

H *G*

2nd CO BE


(Rel. E_0) *(0)* *(5)* *(9)* *(30)* *(57)* *(106)*

Immobile B.E.	−98	−114	−98	−113	−89	−103	−72	−91	−40	−66	6	−14
Mobile B.E.	***−98***	***−114***	***−94***	***−109***	***−89***	***−102***	***−69***	***−87***	***−40***	***−59***	***7***	***−13***

H *G*

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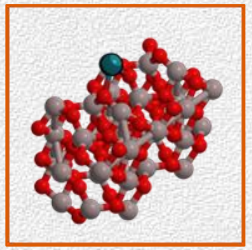
Energies in kJ mol^{-1}, 573 K, 1 bar

2CO on γ-Al_2O_3 (010)

Oxides studied:
(DFT)

γ-Al_2O_3 (010)

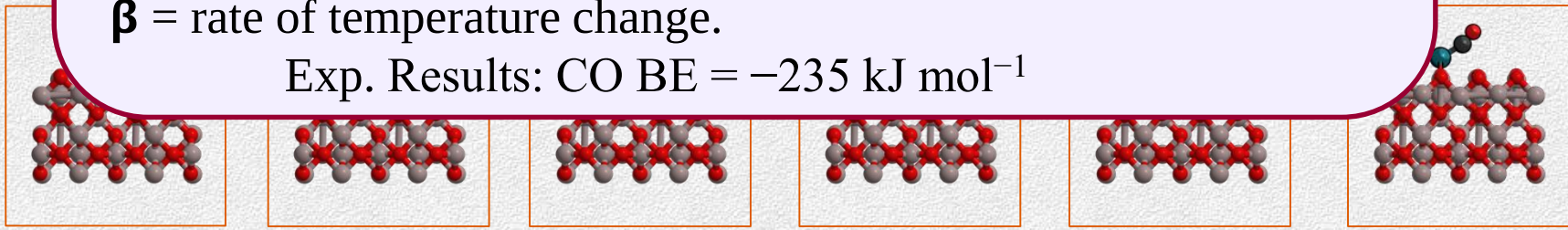
Rh	3-fold
1st CO BE (G)	−266
2nd CO BE (G)	−114



(Rel. E_0) (0)

Redhead analysis: $$\frac{E}{RT_p} = ln\left(\frac{vT_p}{\beta}\right) - 3.64$$

E = kJ/Kmol
T_p = temperature at peak desorption rate
R = ideal gas constant
v = rate constant found in literature for first order CO/Rh
β = rate of temperature change.
Exp. Results: CO BE = −235 kJ mol^{-1}



2nd CO BE												
(Rel. E_0)	(0)		(5)		(9)		(30)		(57)		(106)	
Immobile B.E.	−98	−114	−98	−113	−89	−103	−72	−91	−40	−66	6	−14
Mobile B.E.	*−98*	*−114*	*−94*	*−109*	*−89*	*−102*	*−69*	*−87*	*−40*	*−59*	*7*	*−13*
	H	G										

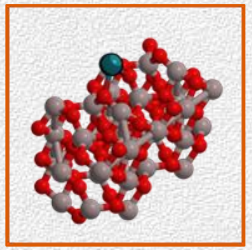
Energies in kJ mol^{-1}, 573 K, 1 bar

2NO on γ-Al_2O_3 (010)

Oxides studied:
(DFT)

γ-Al_2O_3 (010)

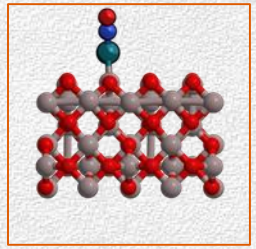
Rh	3-fold
1st CO BE (G)	−266
2nd CO BE (G)	−114
1st NO BE (G)	−359
2nd NO BE(G)	−119



(Rel. E_0) *(0)*

(Rel. E_0) *(0)*

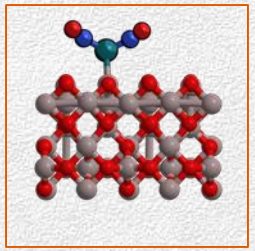
Mobile B.E. 1st CO BE ***−345*** ***−359***
H *G*

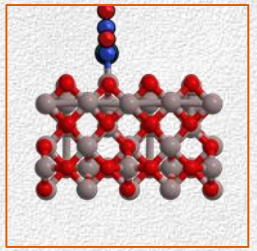


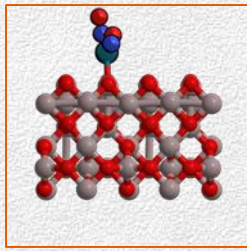
(9)

−363 ***−350***

2nd CO BE







(Rel. E_0)	*(0)*		*(15)*		*(18)*		*(21)*		*(28)*		*(50)*	
Immobile B.E.	−96	−119	−82	−105	−79	−103	−84	−98	−68	−91	−46	−69
Mobile B.E.	***−96***	***−119***	***−80***	***−103***	***−77***	***−101***	***−75***	***−105***	***−68***	***−91***	***−45***	***−69***
	H	*G*										

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Energies in kJ mol^{-1}, 573 K, 1 bar

Exchange energies γ-Al_2O_3 (010)

Oxides studied:
(DFT)

γ-Al_2O_3 (010)

Rh	3-fold
1st CO BE (G)	−266
2nd CO BE (G)	−114
1st NO BE (G)	−359
2nd NO BE(G)	−119

Exchange Energies

$CO^* + NO(g) \rightarrow NO^* + CO(g)$

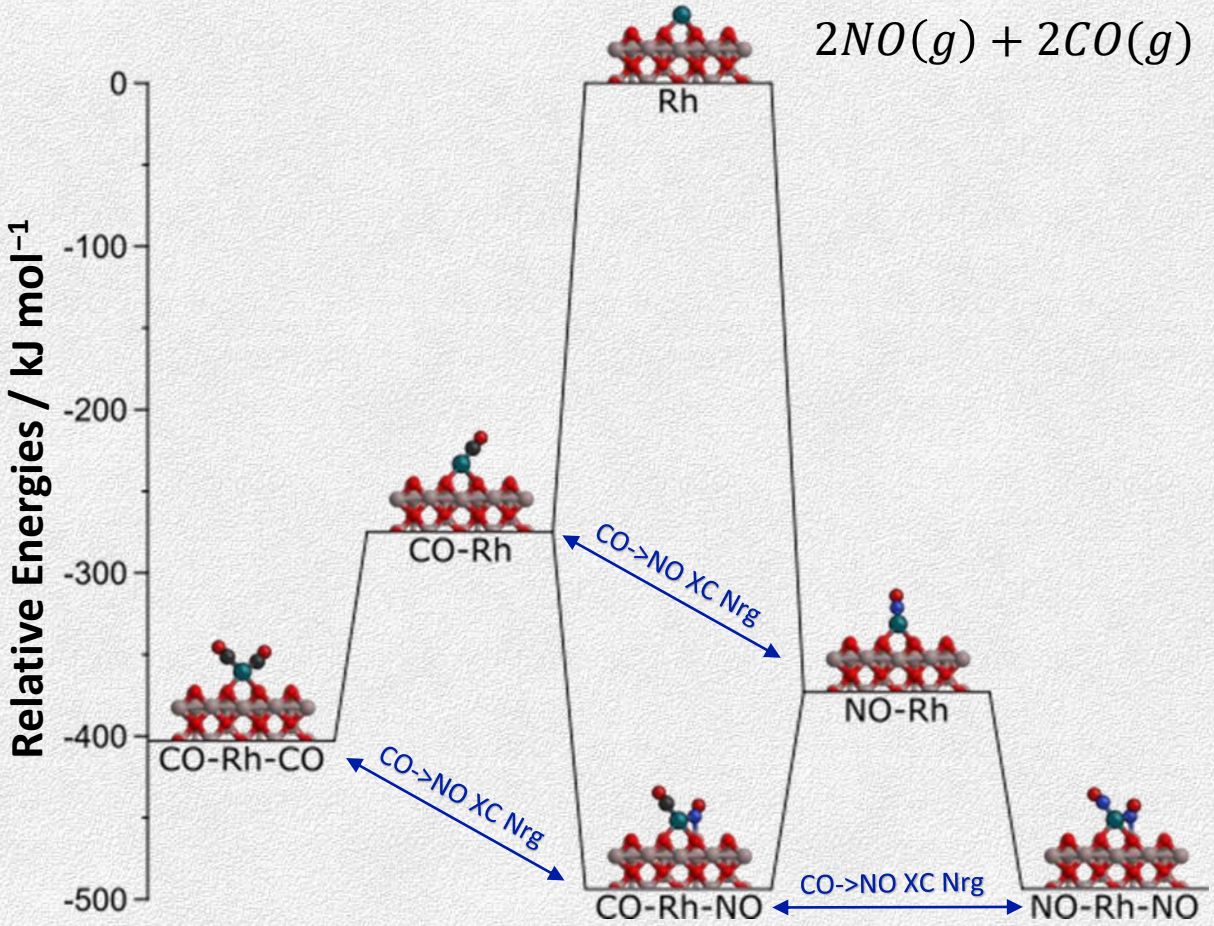
−93 kJ mol^{-1}

$CO^* + CO^* + NO(g) \rightarrow CO^* + NO^* + CO(g)$

−83 kJ mol^{-1}

$NO^* + CO^* + NO(g) \rightarrow NO^* + NO^* + CO(g)$

−5 kJ mol^{-1}



Energies in kJ mol^{-1}, 573 K, 1 bar

Future work

Oxides studied:
(DFT)

γ-Al_2O_3 (010)

Rh	3-fold
1st CO BE (G)	−266
2nd CO BE (G)	−114
1st NO BE (G)	−359
2nd NO BE(G)	−119

Exchange Energies

$CO^* + NO(g) \rightarrow NO^* + CO(g)$

−93 kJ mol^{-1}

$CO^* + CO^* + NO(g)$
$\rightarrow CO^* + NO^* + CO(g)$

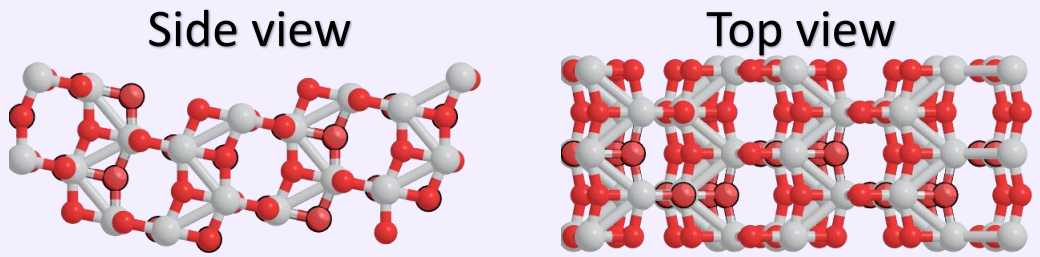
−83 kJ mol^{-1}

$NO^* + CO^* + NO(g)$
$\rightarrow NO^* + NO^* + CO(g)$

−5 kJ mol^{-1}

Defect/step sites

(021)



Hydroxyl groups

Thought to cover surface

Facilitate H-assisted pathways

Perform reactions

Energies in kJ mol^{-1}, 573 K, 1 bar

Recap

Produce more chemicals and fuels

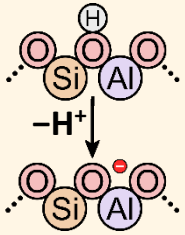
Using less energy

Carbon neutral way

Reduce emissions and pollution

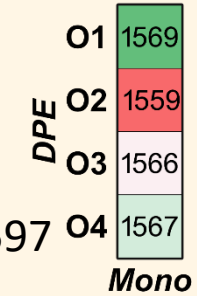
Catalyst can solve these issues

DPE in CHA



Isolated: 1568

Paired: 1551–1597

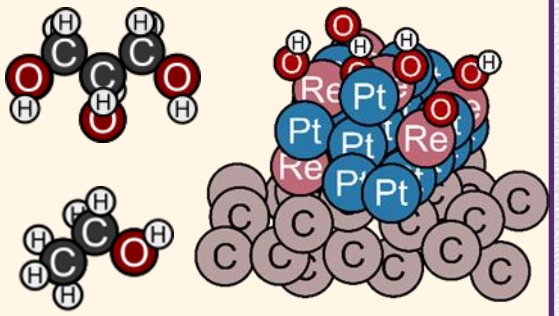


Methanol dehydration

Isolated: Associative
Sites covered in methanol

Paired: Rates increased

Alcohols on metals



Rates $PtReO_x$>$AuReO_x$>Pt

Rates ethanol > glycerol

ReO_x
Promotes 1°C–O cleavage
Facilitates 2°C–O cleavage
Reduces C–C cleavage

$AuReO_x$ produces unsaturated compounds

Atomic Rh
(3-way converter)

γ-Al_2O_3 (010)

Rh	3-fold
1st CO BE (G)	−266
2nd CO BE (G)	−114
1st NO BE (G)	−359
2nd NO BE(G)	−119

Exchange Energies

$CO^* + NO(g) \rightarrow NO^* + CO(g)$

−93 kJ mol^{-1}

$CO^* + CO^* + NO(g)$
$\rightarrow CO^* + NO^* + CO(g)$

−83 kJ mol^{-1}

$NO^* + CO^* + NO(g)$
$\rightarrow NO^* + NO^* + CO(g)$

−5 kJ mol^{-1}

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Energies in kJ mol^{-1}

Acknowledgements

Hibbitts Research Group

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HiPerGator 2.0
The University of Florida Supercomputer

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PURDUE UNIVERSITY

Ford

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