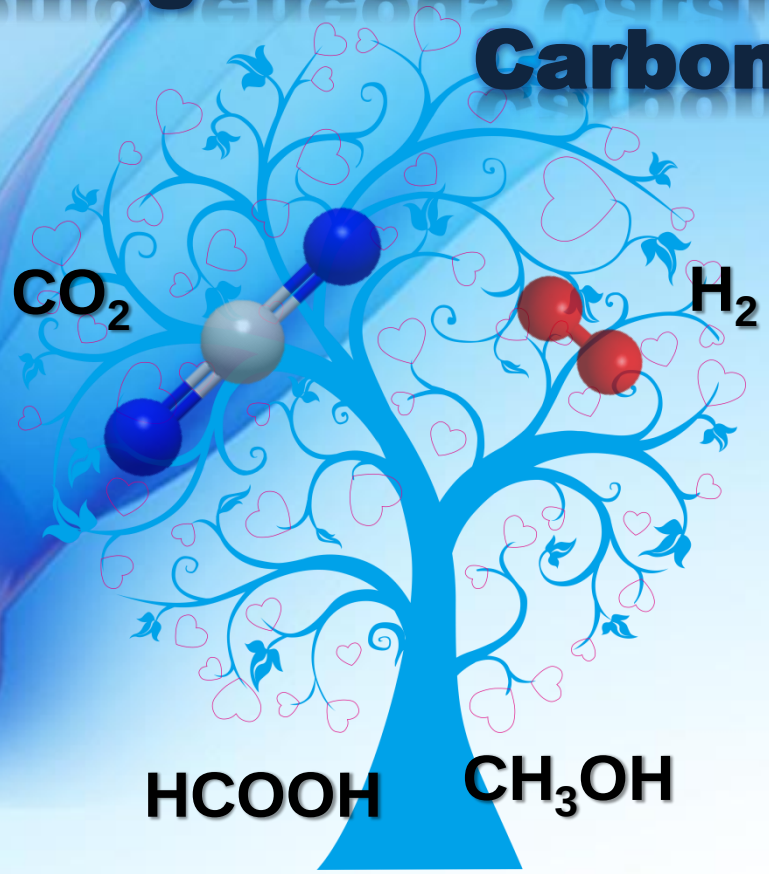
Millstones in the Glorious Road:

Homogeneous Catalytic Hydrogenation of Carbon Dioxide



Fanzhou Jiang

2014-03-24

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Introduction: Utilization of Carbon Dioxide

Hydrogenation of Carbon Dioxide to Formic Acid

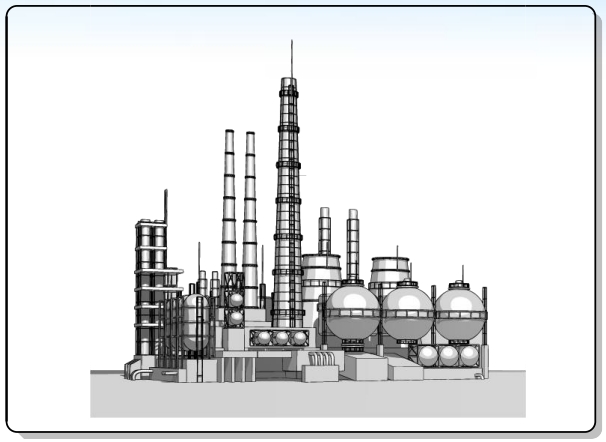
Hydrogenation of Carbon Dioxide to Methanol

Summary and Outlook

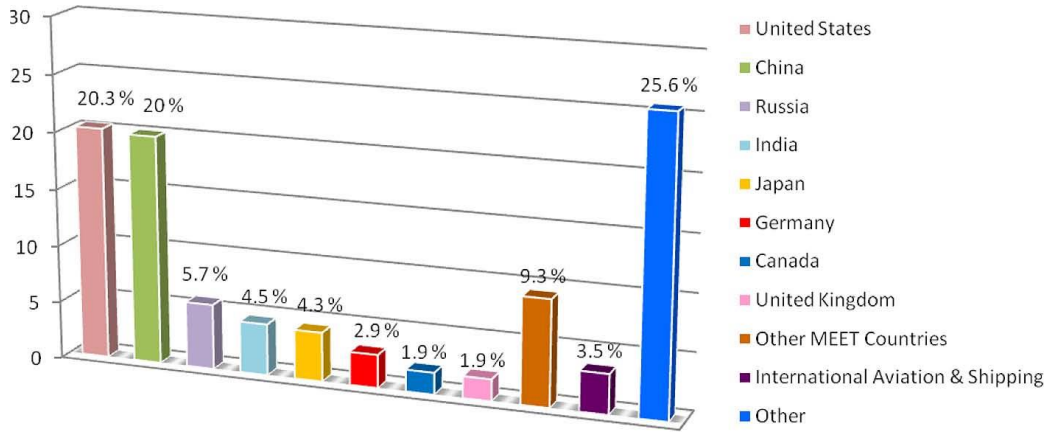
Introduction: Utilization of Carbon Dioxide

coal, 43%

oil, 36%



gas, 20%



Emission of CO_2 per country and from the avio-sector

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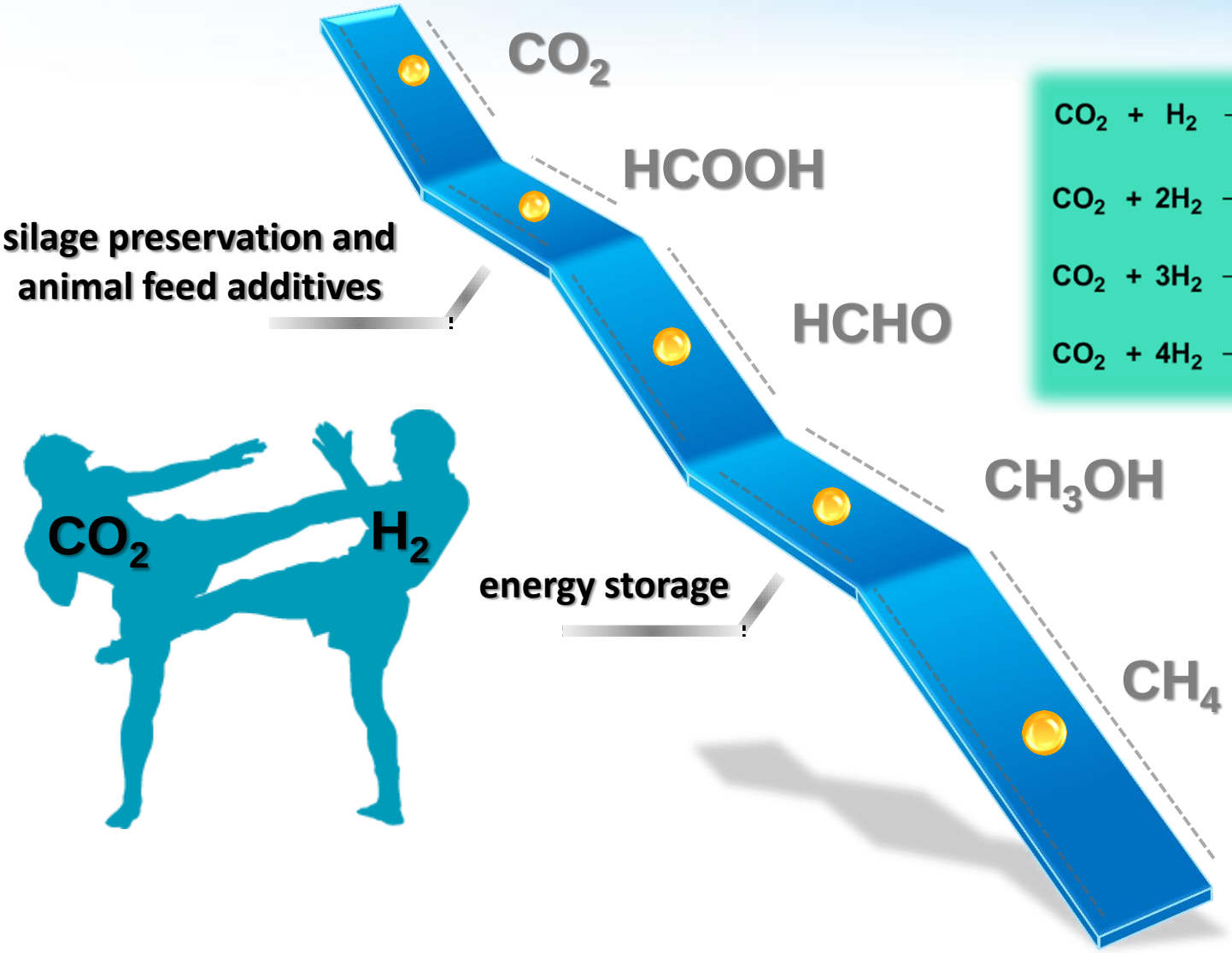
Introduction: Utilization of Carbon Dioxide



$$CO_2 + H_2 \xrightarrow{\text{cat.}} HCOOH$$

$$CO_2 + 2H_2 \xrightarrow{\text{cat.}} HCHO$$

$$CO_2 + 3H_2 \xrightarrow{\text{cat.}} CH_3OH$$

$$CO_2 + 4H_2 \xrightarrow{\text{cat.}} CH_4$$

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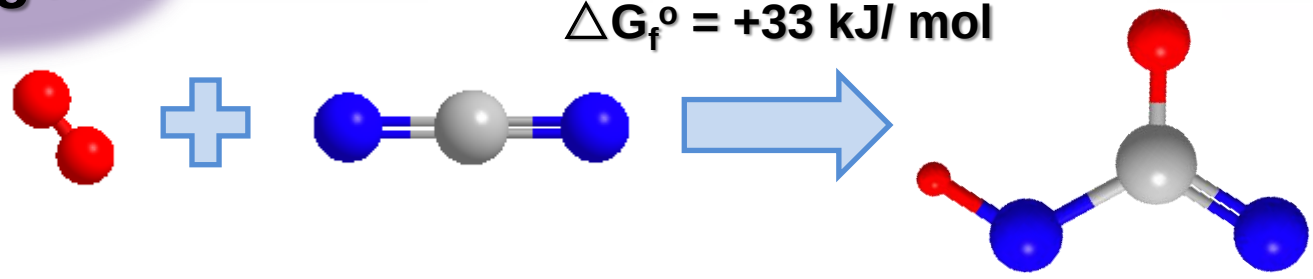
Hydrogenation of Carbon Dioxide to Formic Acid

endoergonic

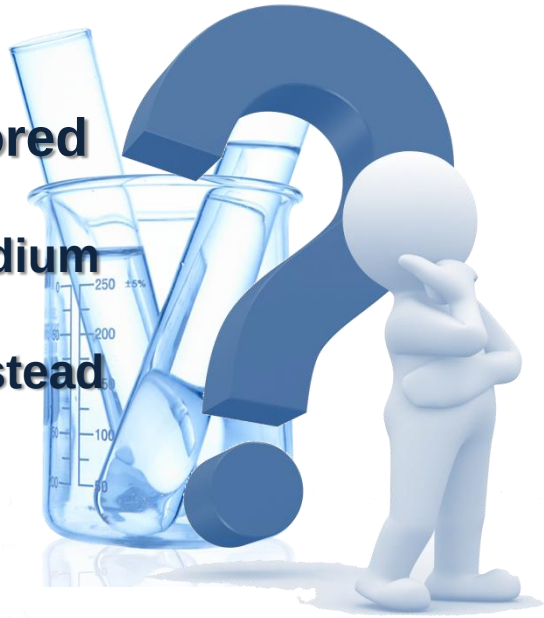
$\triangle G_f^o$ = +33 kJ/ mol



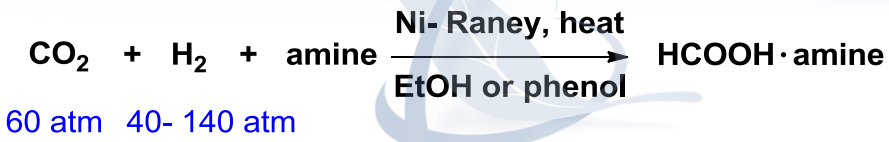
H_2 (gas) CO_2 (gas) HCOOH (liquid)

make the themodynamics of the process favored

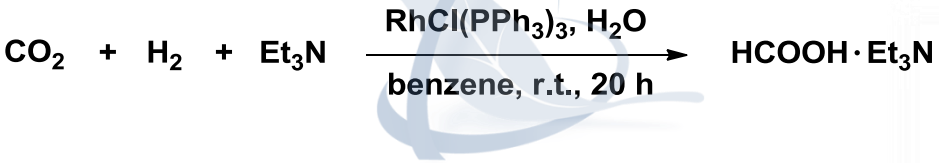
- **if the reaction is carried out in a condensed medium**
- **If a base is used that produces formate salts instead of free formic acid**



Hydrogenation of Carbon Dioxide to Formic Acid

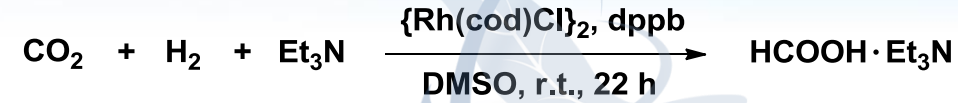


Farlow, M. W.; Adkins, H. *J. Am. Chem. Soc.* **1935**, *57*, 2222.



Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, 5, 863.

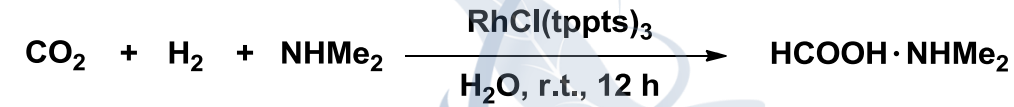
Hydrogenation of Carbon Dioxide to Formic Acid



20 bar 20 bar

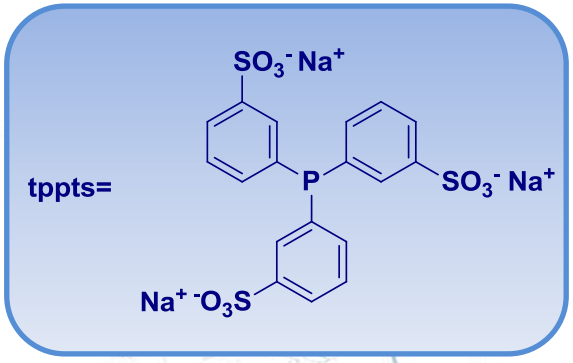
TON= 1150, TOF= 52 h^{-1}

Graf, E.; Leitner, W. *J. Chem. Soc., Chem. Comm.* **1992**, 623.



20 bar 20 bar

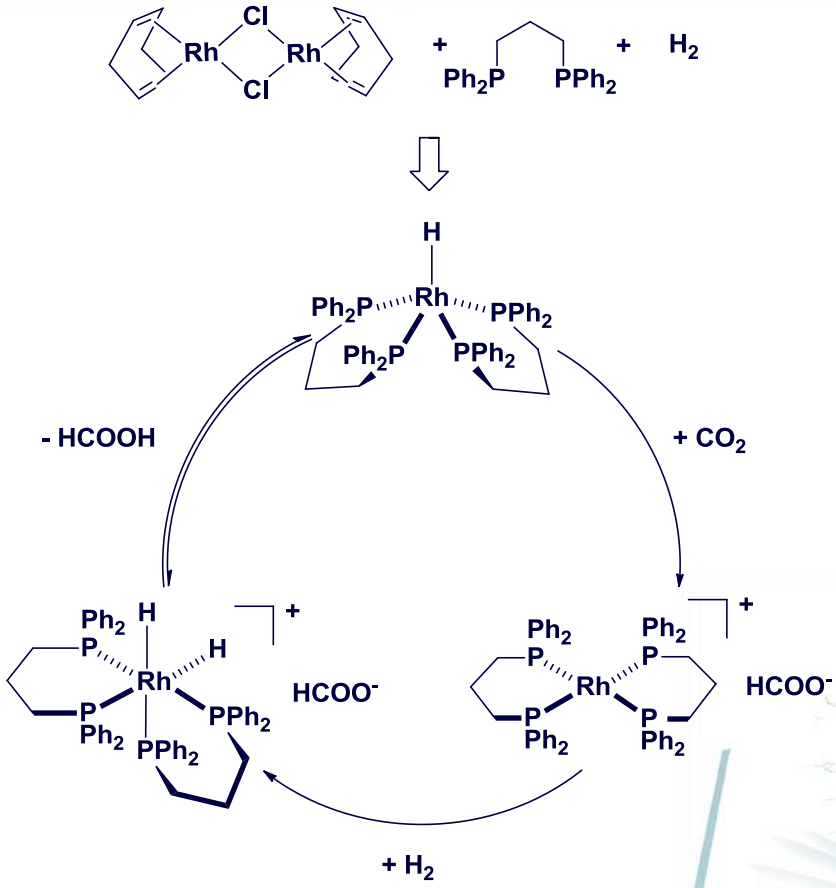
TON= 3439, TOF= 287 h^{-1}



Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Comm.* **1993**, 1465.

Hydrogenation of Carbon Dioxide to Formic Acid

Proposed Mechanism



Burgemeister, T.; Kastner, F.; Leitner, W. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 739.

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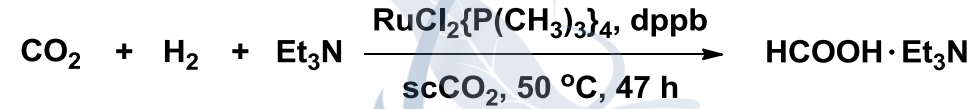
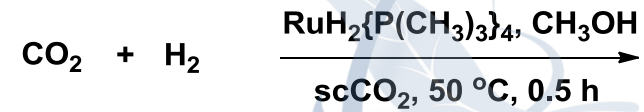
Hydrogenation of Carbon Dioxide to Formic Acid



85 bar 120 bar

TON= 7200, TOF= 150 h^{-1}

Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231.



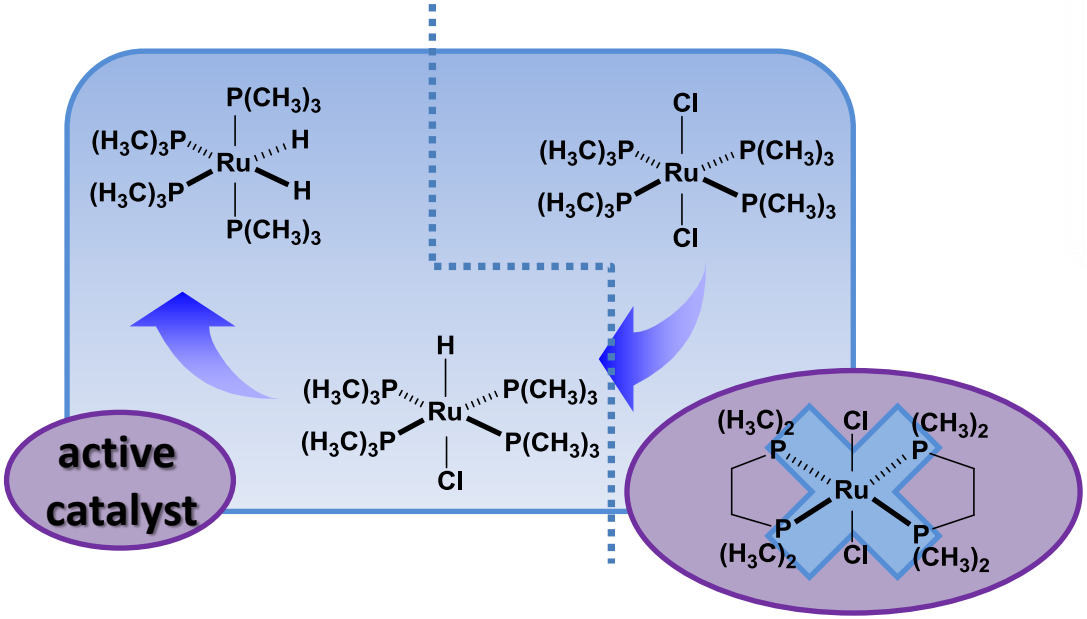
80 bar 120 bar

TON= 2000, TOF= 4000 h^{-1}

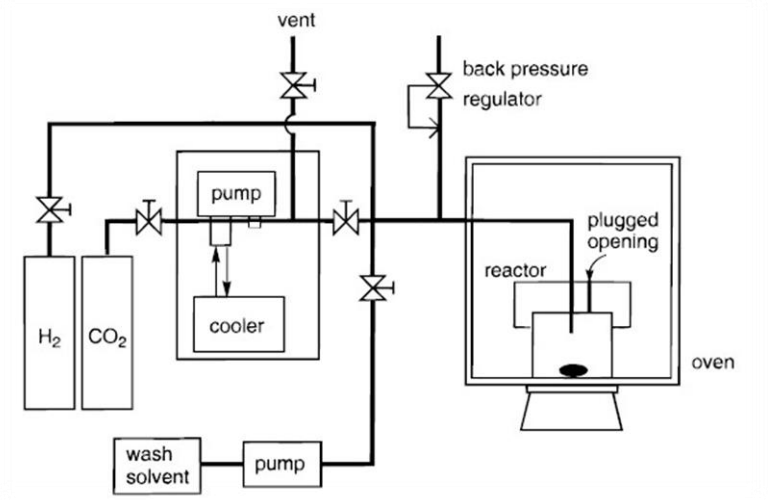
Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

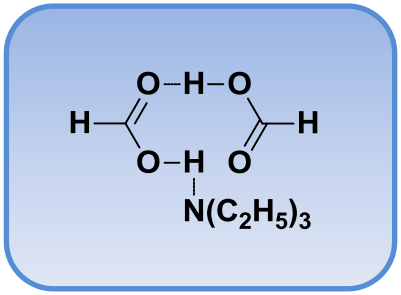
Hydrogenation of Carbon Dioxide to Formic Acid

Reactions in SCFs are strongly affected by phase changes



Equipment used for the reactions in $scCO_2$



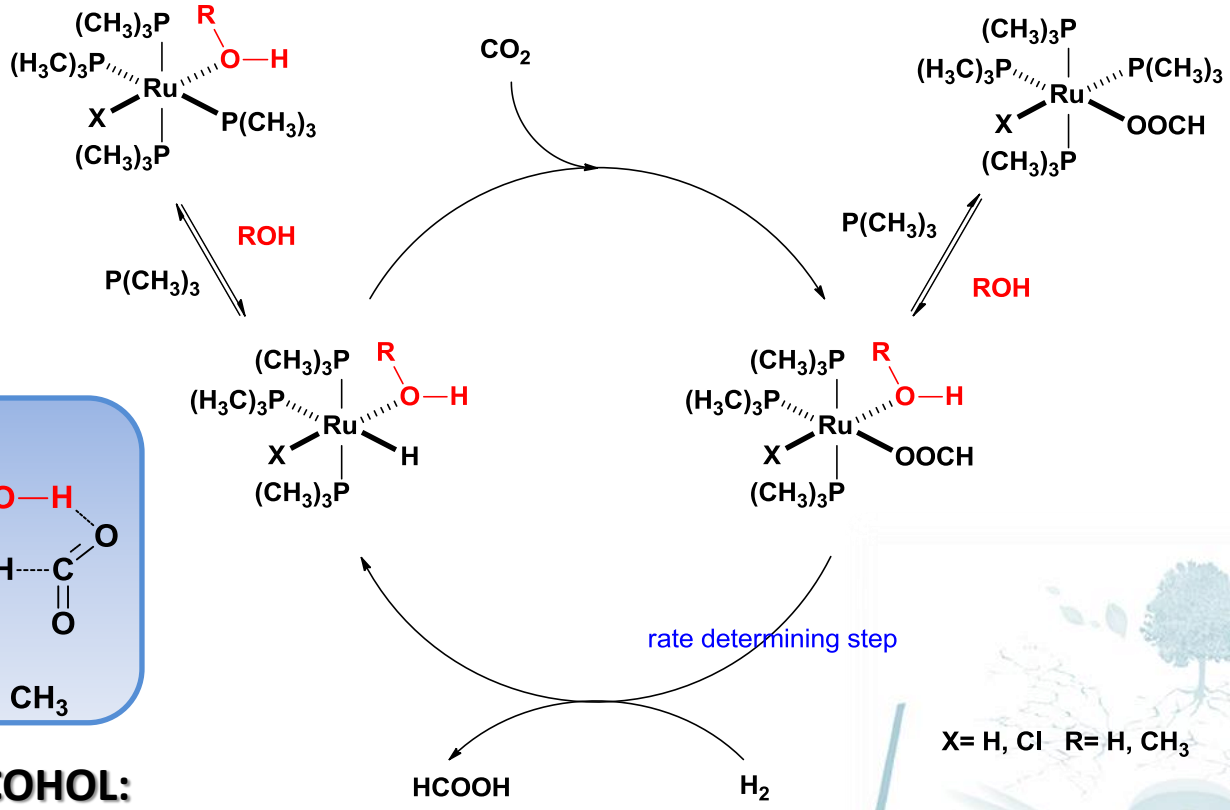


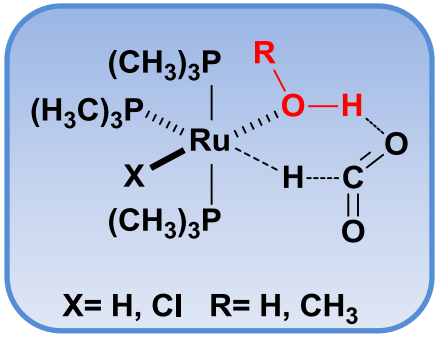
Stable 2:1 adducts

Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

Hydrogenation of Carbon Dioxide to Formic Acid

Proposed Mechanism





WATER or ALCOHOL: hydrogen bonding

X= H, Cl R= H, CH_3

Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

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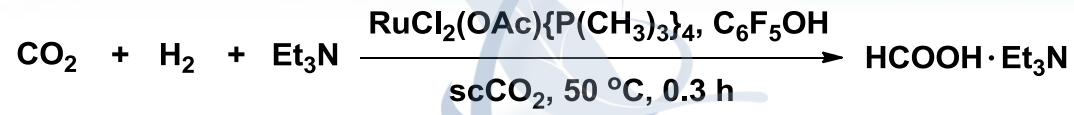
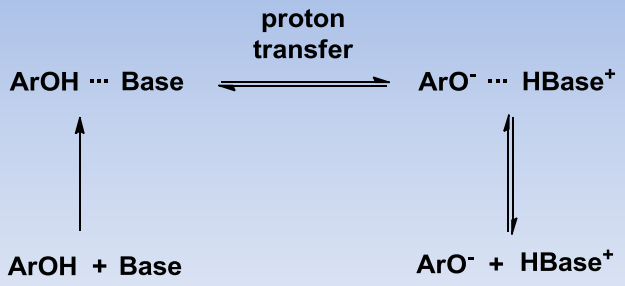
Hydrogenation of Carbon Dioxide to Formic Acid



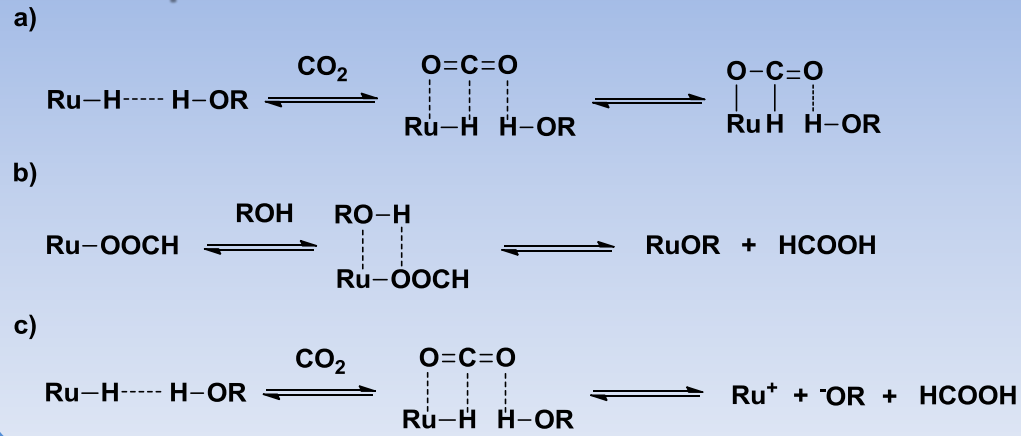
70 bar 120 bar

TON= 28500, TOF= 95000 h^{-1}

proton-transfer equilibrium

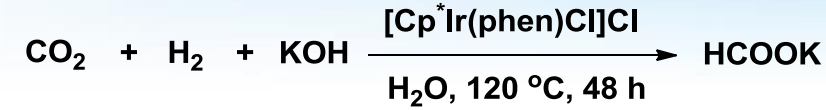


possible roles of an acidic alcohol



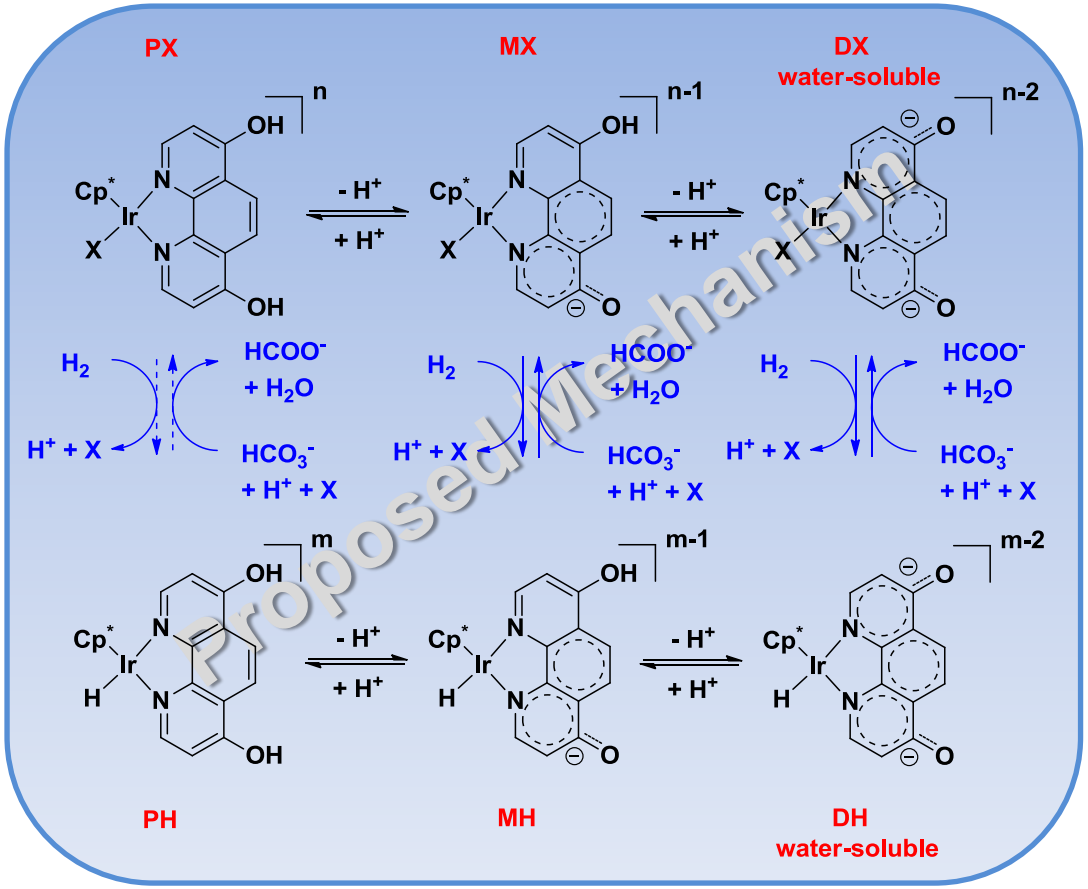
Munshi, P.; Main, A. D.; Linehan, J. C.; Tai, C.-C.; Jessop, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 7963.

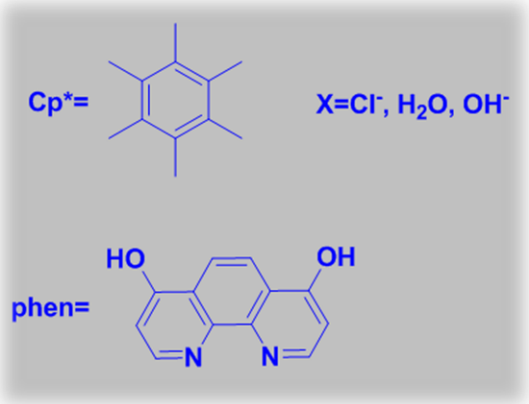
Hydrogenation of Carbon Dioxide to Formic Acid



30 bar 30 bar

TON= 220000, TOF= 33000 h^{-1}





Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H.; Kasuga, K. *Organometallics* **2007**, *26*, 702.

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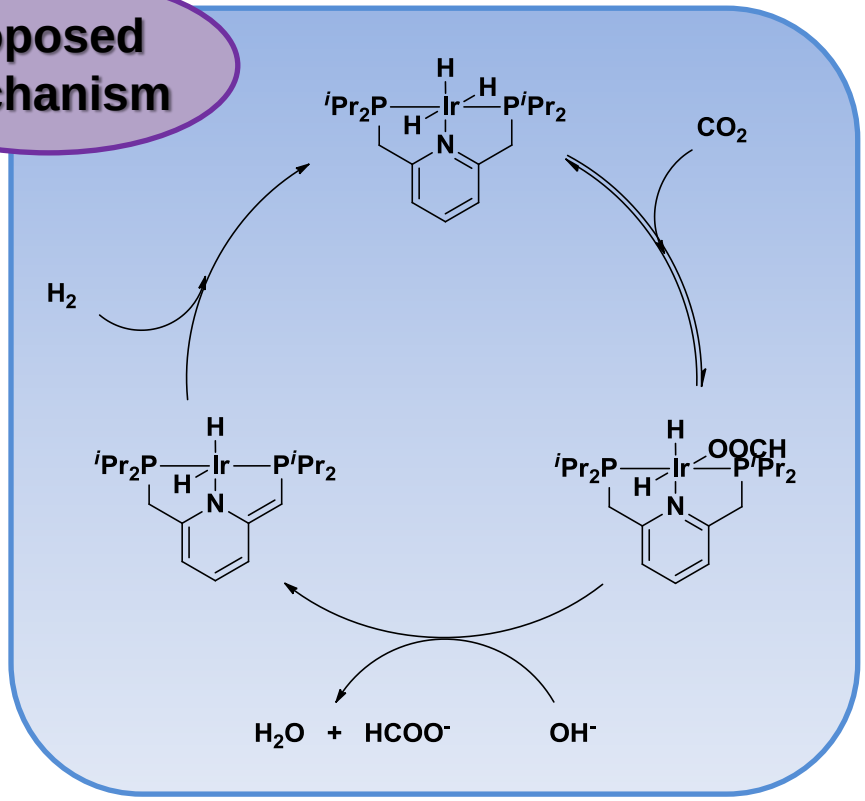
Hydrogenation of Carbon Dioxide to Formic Acid

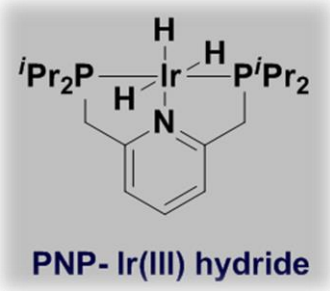
$$CO_2 + H_2 + KOH \xrightarrow[H_2O,\ 120\ ^oC,\ 48\ h]{\text{PNP-Ir(III) hydride}} HCOOK$$

30 bar 30 bar

TON= 3500000, TOF= 73000 h^{-1}

Proposed Mechanism





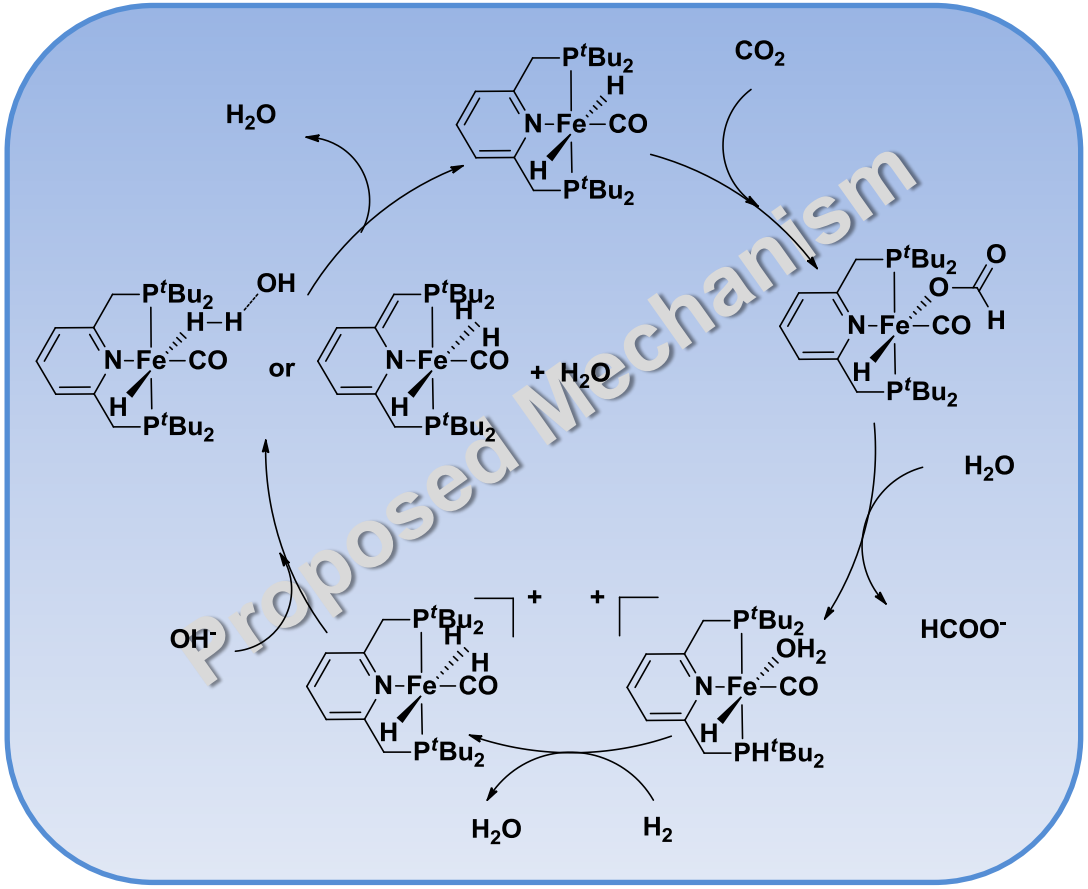
Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168.

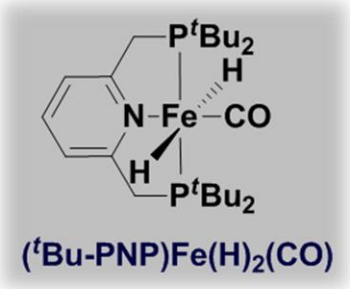
Hydrogenation of Carbon Dioxide to Formic Acid

$$CO_2 + H_2 + NaOH \xrightarrow[H_2O/\ THF,\ 80\ ^oC,\ 5\ h]{(^tBu\text{-}PNP)Fe(H)_2(CO)} HCOONa$$

3.33 bar 6.66 bar

TON= 788, TOF= 156 h^{-1}





Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 9948.

Hydrogenation of Carbon Dioxide to Formic Acid

$$NaHCO_3 + H_2 \xrightarrow[MeOH,\ 100\ ^oC,\ 20\ h]{Fe(BF_4)_2\cdot 6H_2O,\ P(p\text{-}PPh_2)_3} HCOONa$$

60 bar

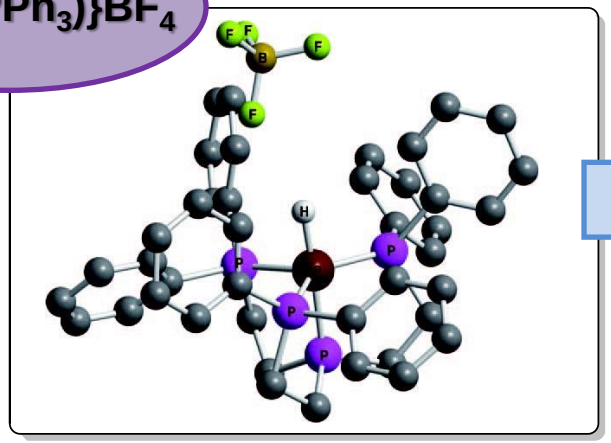
TON= 7546

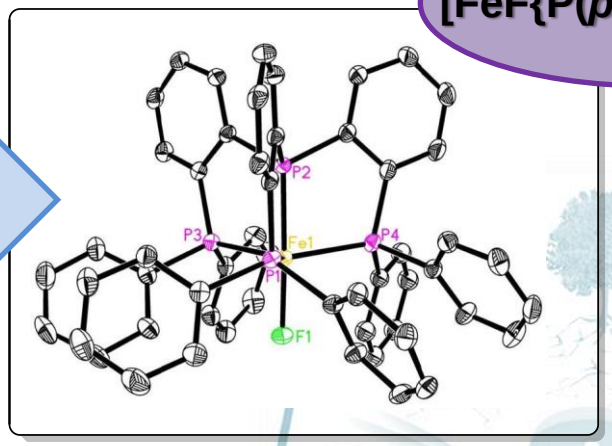
$$CO_2 + H_2 + NHMe_2 \xrightarrow[MeOH,\ 100\ ^oC,\ 20\ h]{Fe(BF_4)_2\cdot 6H_2O,\ P(p\text{-}PPh_2)_3} HCONMe_2$$

30 bar 70 bar

TON= 5104

$\{FeH(PPh_3)\}BF_4$





$[FeF\{P(p\text{-}PPh_2)_3\}]BF_4$

Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9777.

Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 20701.

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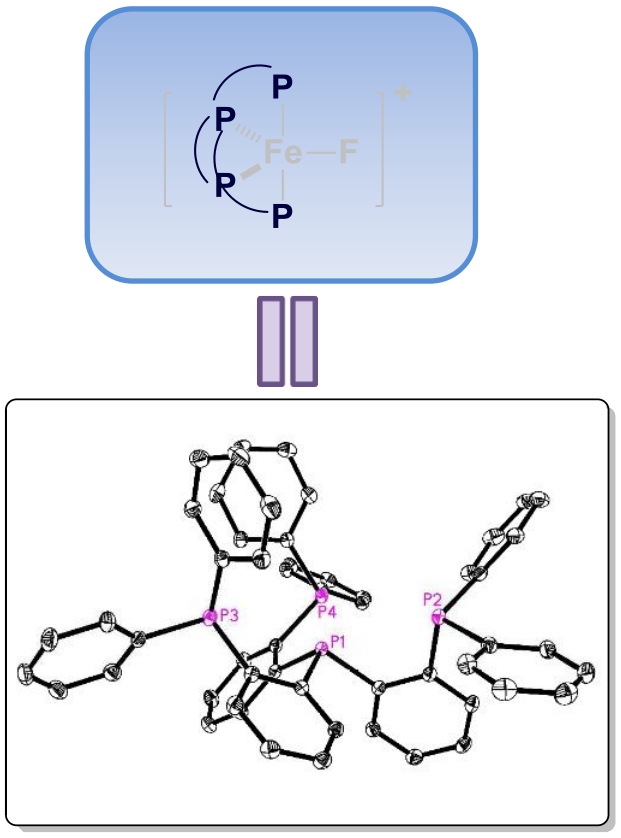
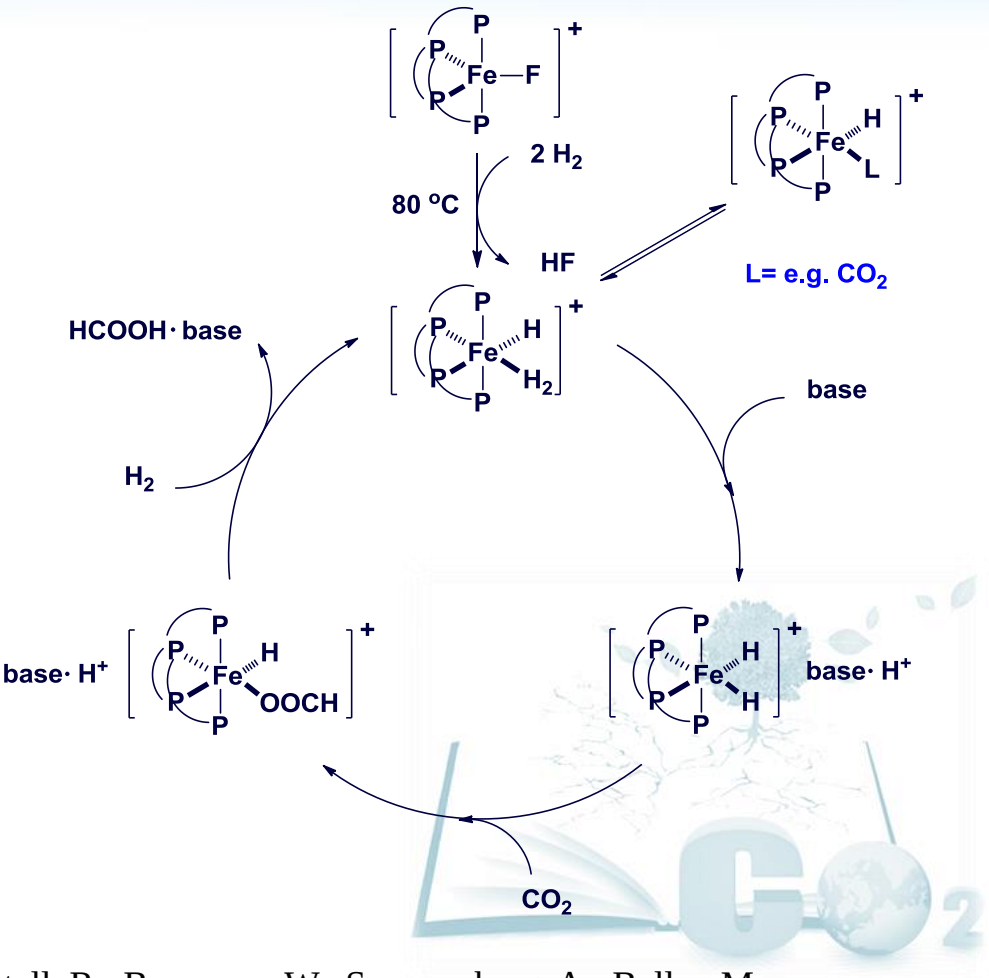
Hydrogenation of Carbon Dioxide to Formic Acid

Proposed Mechanism





Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 20701.

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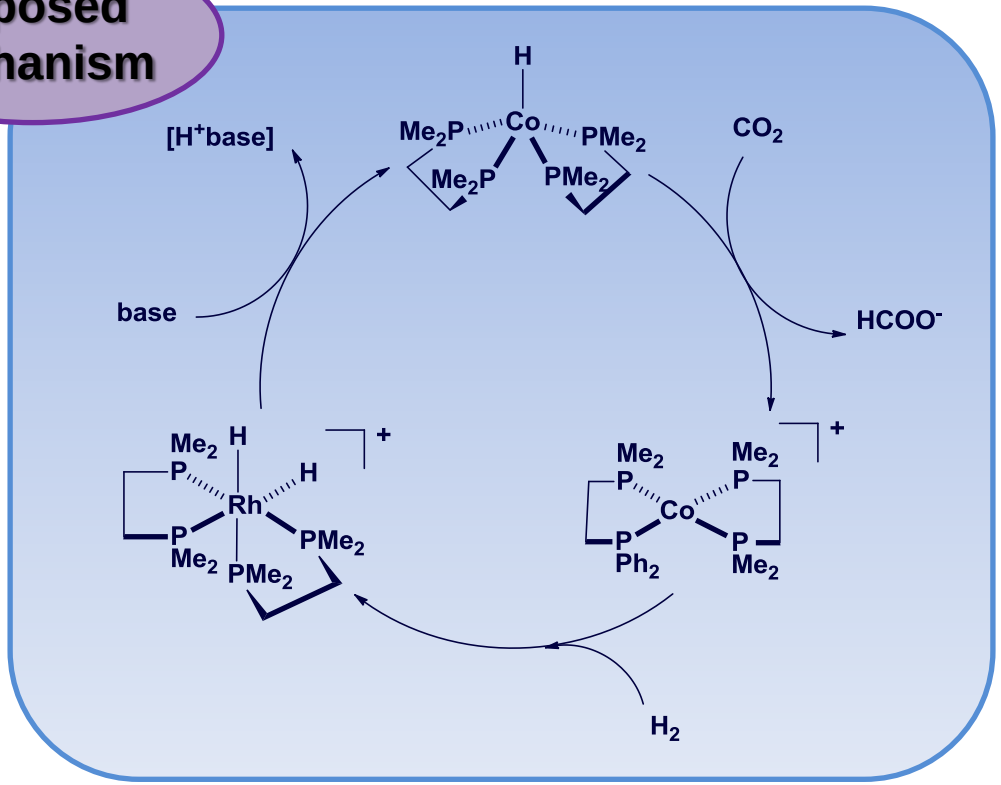
Hydrogenation of Carbon Dioxide to Formic Acid

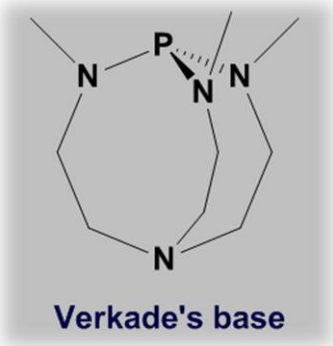
$$CO_2 + H_2 + \text{base} \xrightarrow[\text{THF, r.t., 1 h}]{\text{Co(dmpe)}_2\text{H}} \text{HCOOH} \cdot \text{base}$$

10 bar 10 bar

TON= 74000, TOF= 9400 h^{-1}

Proposed Mechanism





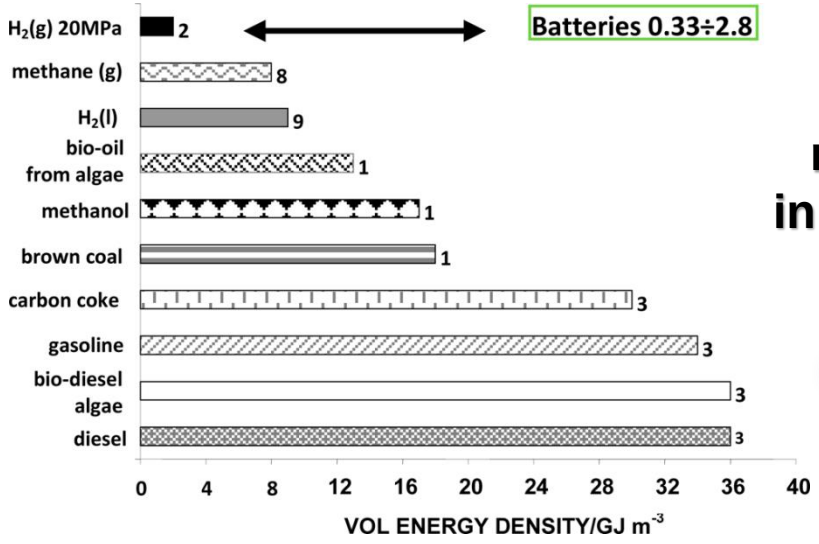
Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 11533.

Hydrogenation of Carbon Dioxide to Methanol

solve the greenhouse effect?

solve the energy exhausted?

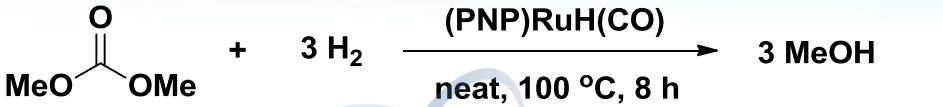
hydrogenation of CO_2



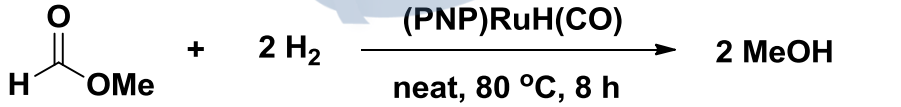
methanol: a high energy density in comparision with that of batteries

storage of electric energy

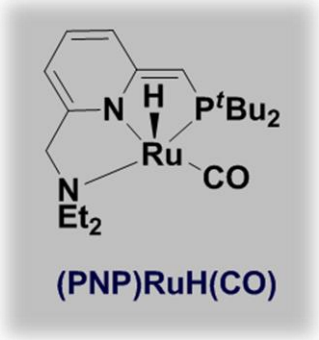
Hydrogenation of Carbon Dioxide to Methanol

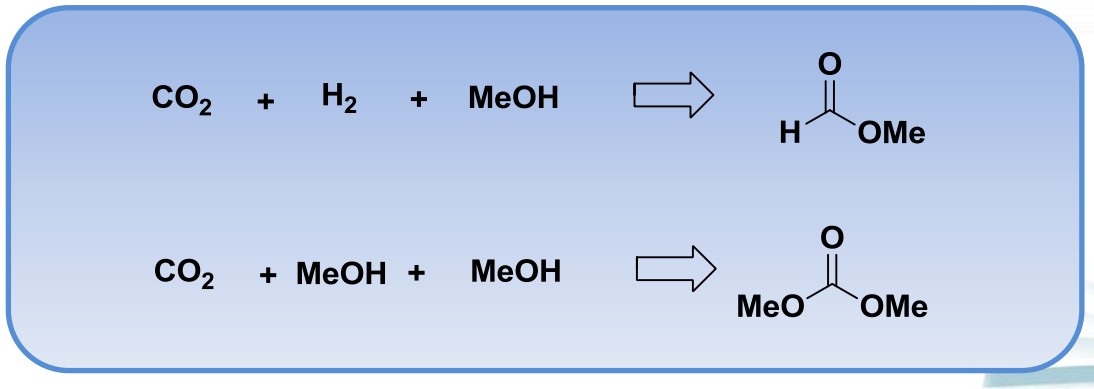


10 atm TON> 990



10 atm TON= 980

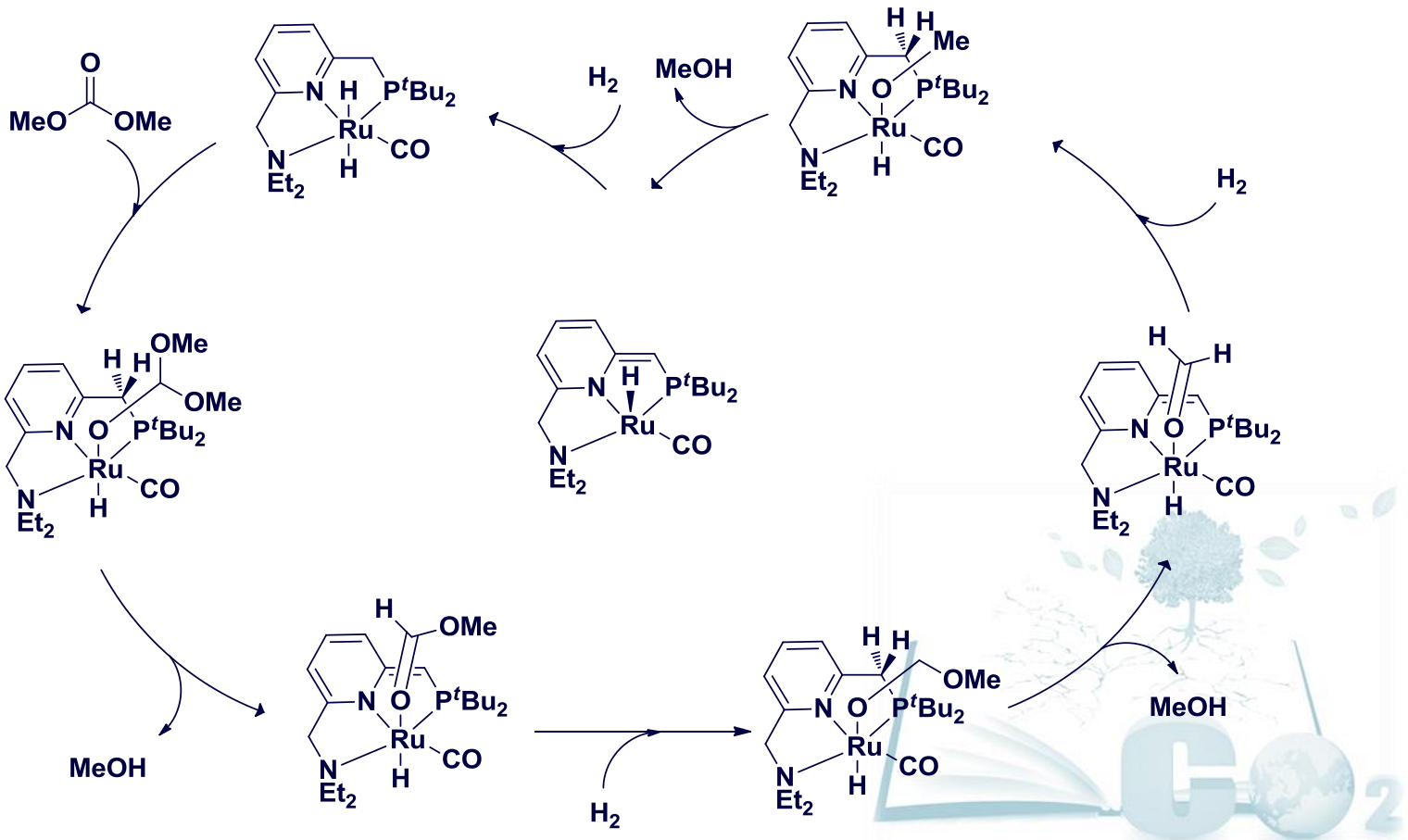




Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609.

Hydrogenation of Carbon Dioxide to Methanol

Proposed Mechanism



Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609.

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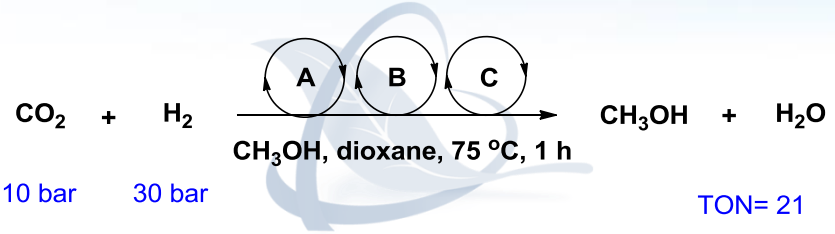
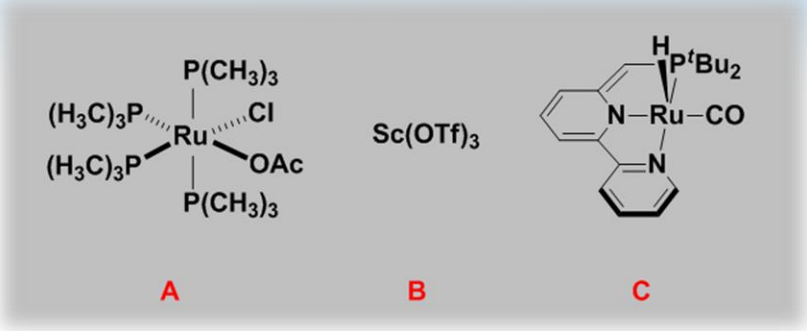
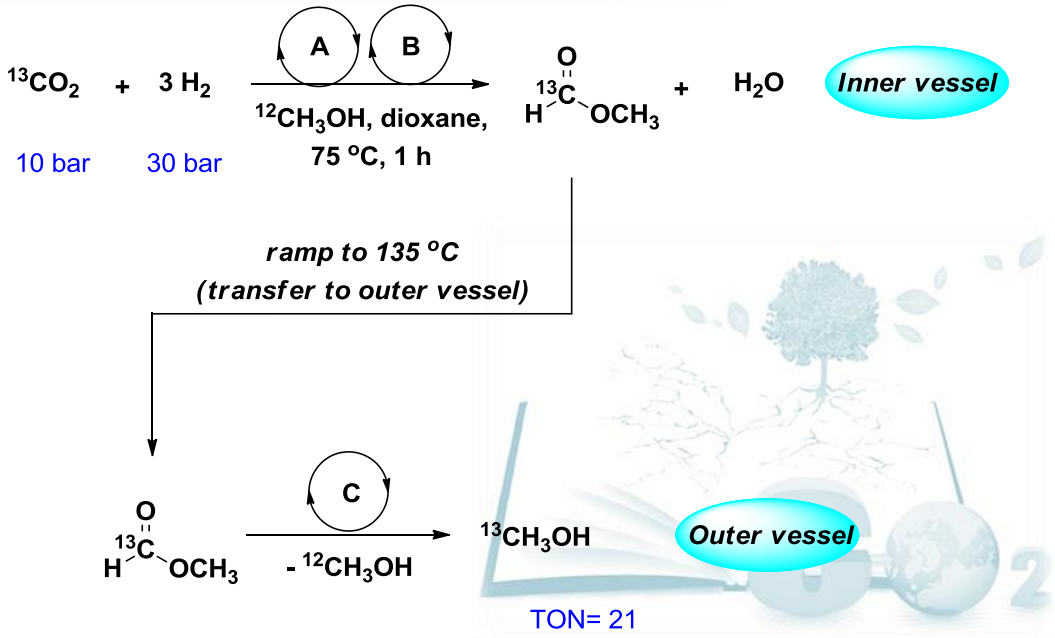
Hydrogenation of Carbon Dioxide to Methanol







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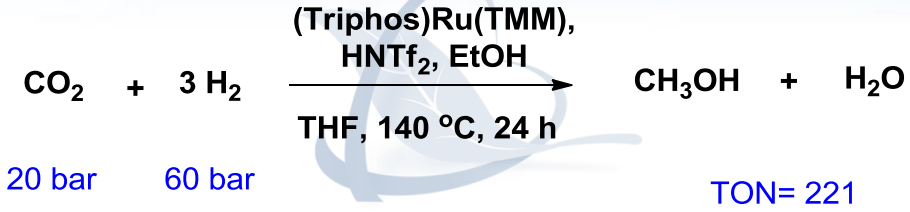
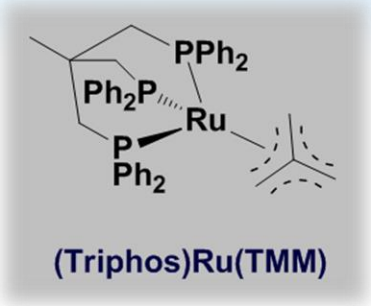
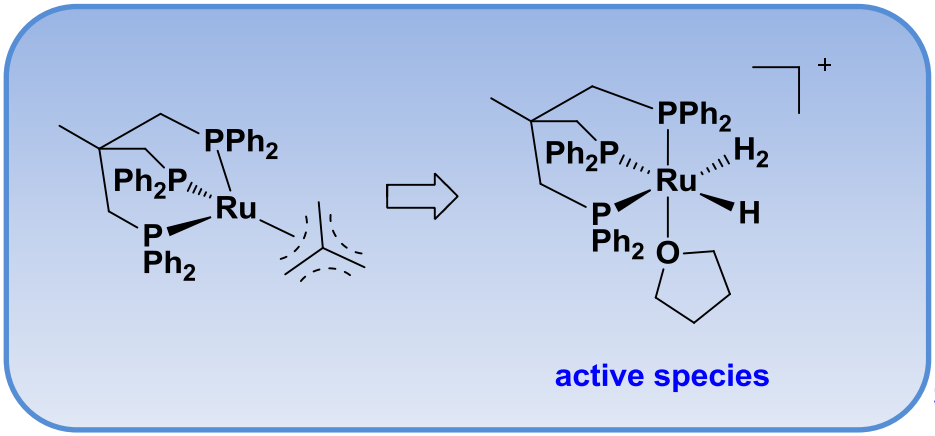
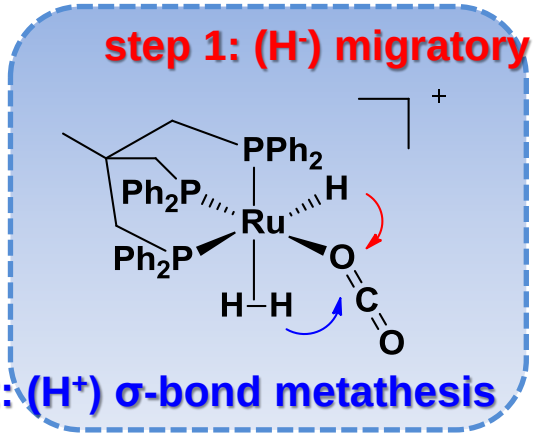
Hydrogenation of Carbon Dioxide to Methanol









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Summary and Outlook

transition-metal catalysts based on rhodium, ruthenium and iridium: high TONs

inexpensive biorelevant metal catalysts such as iron and cobalt: lower activity

efficient catalysis with industrially available feedstocks enriched with CO_2

efficient hydrogenation of CO_3^{2-} or HCO_3^-

more energy efficient reduction processes of CO_2


Thank you !