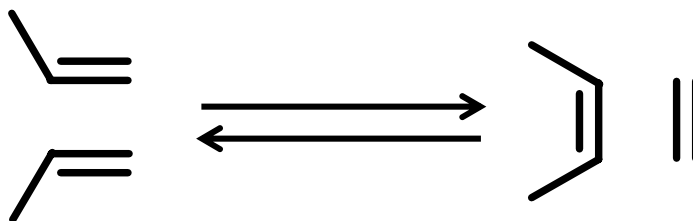
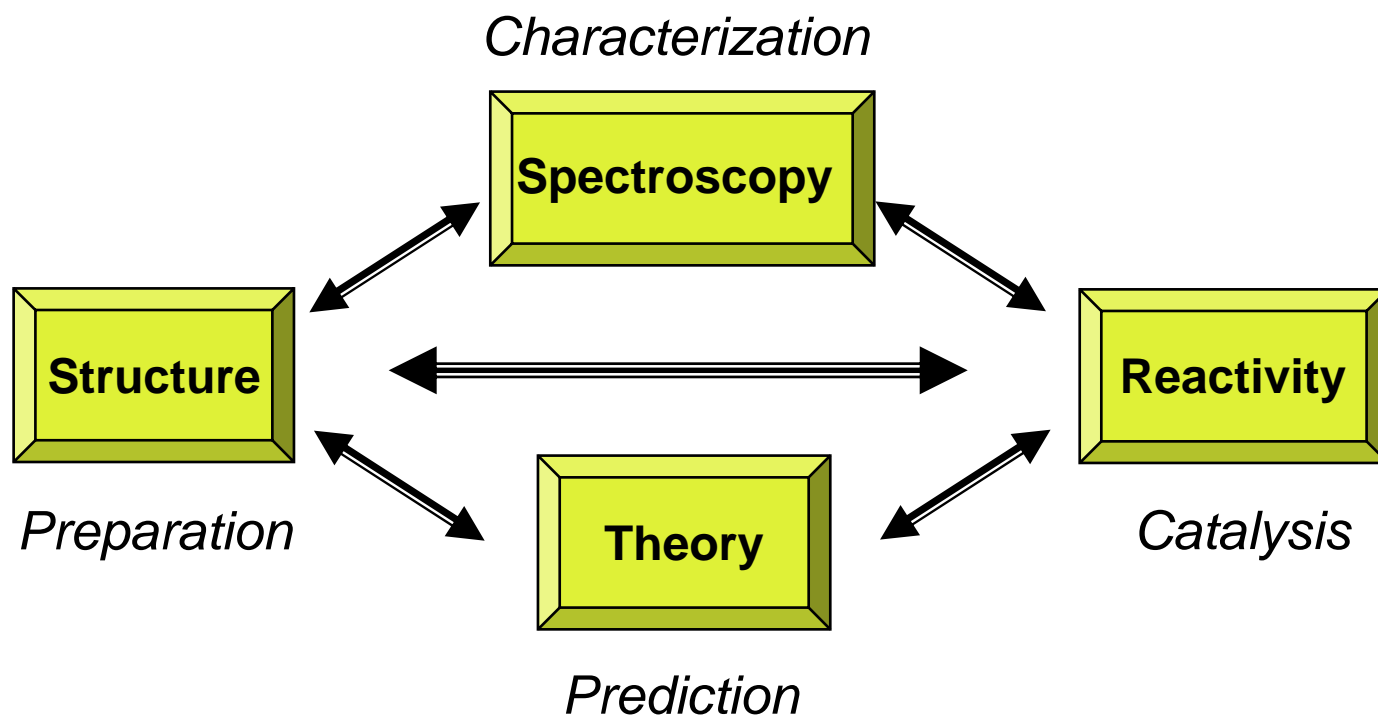


Laboratoire de Chimie Organométallique de Surface

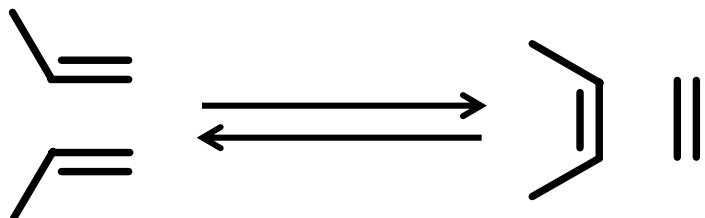
*A Molecular Approach to the Design and the Understanding
of Heterogeneous Olefin Metathesis Catalysts*



e-mail : coperet@cpe.fr

Development of olefin metathesis catalysts

Heterogeneous catalysis



$\text{MoO}_3/\text{SiO}_2$ or Al_2O_3 (150-200°C)

Phillips Petroleum

WO_3/SiO_2 or Al_2O_3 (400-450°C)

Phillips Petroleum

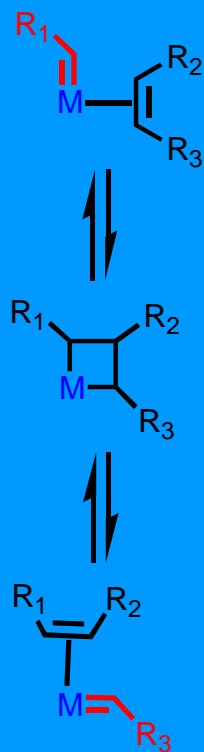
$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ (25-100°C)

BP Chemicals

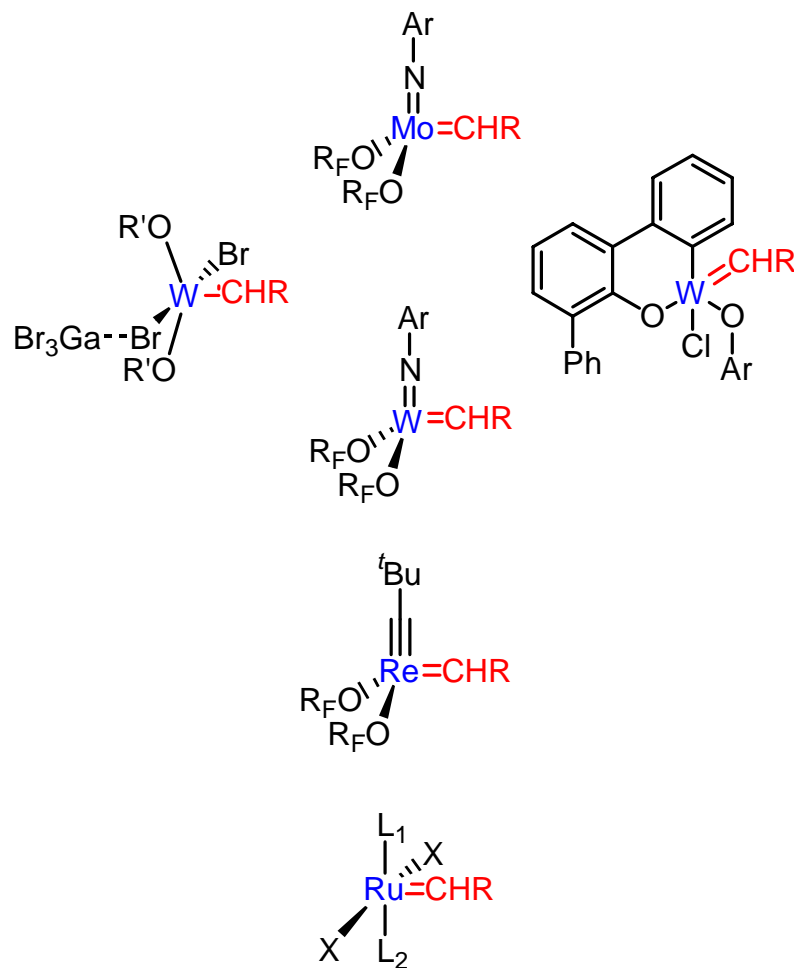
- Regeneration possible
- Not compatible with functional groups

SOMC

SOMC



Homogeneous catalysis



Selective catalysts
Compatible with functional groups

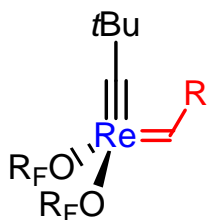
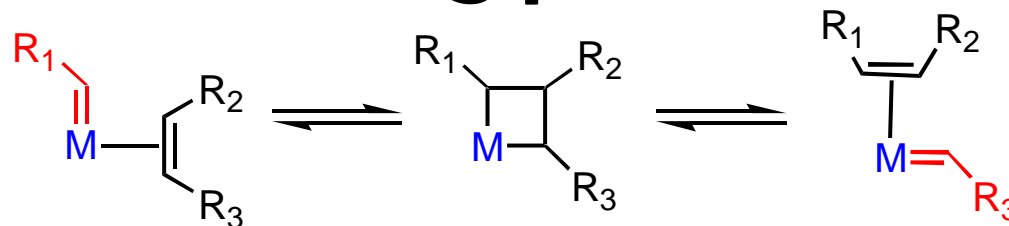
Surface Organometallic Chemistry :

An approach combining the advantages of homogeneous and heterogeneous catalysis

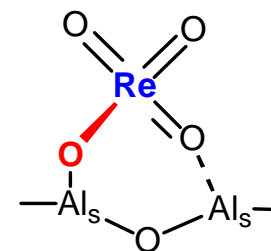
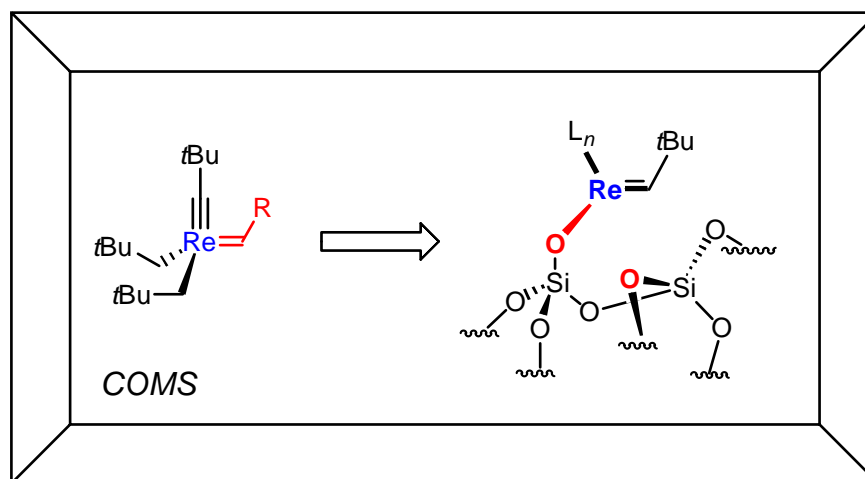
Homogeneous Catalysis

SOMC

Heterogeneous Catalysis



100% of active site



Proposed active site for

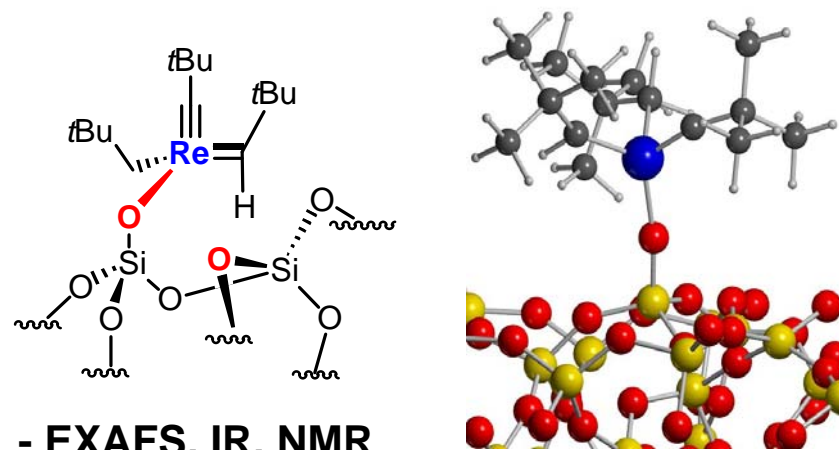
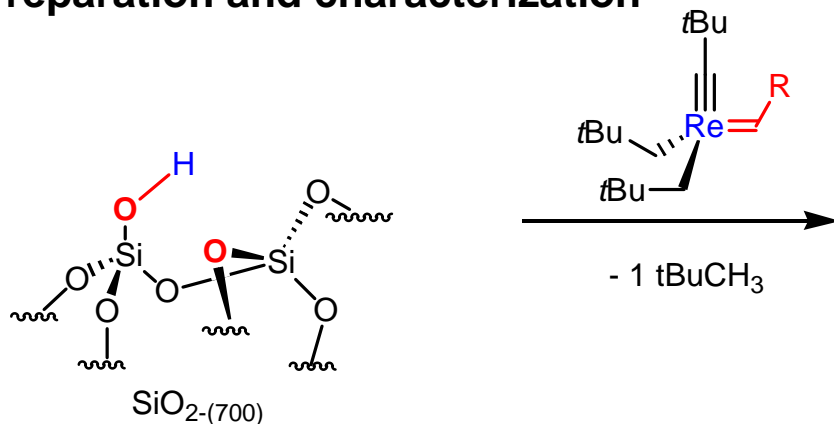
$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$

2% of active site

M. Chabanas *et al.* *J. Am. Chem. Soc.* **2001**, *123*, 2062.
C. Copéret *New J. Chem.* **2004**, *28*, 1.

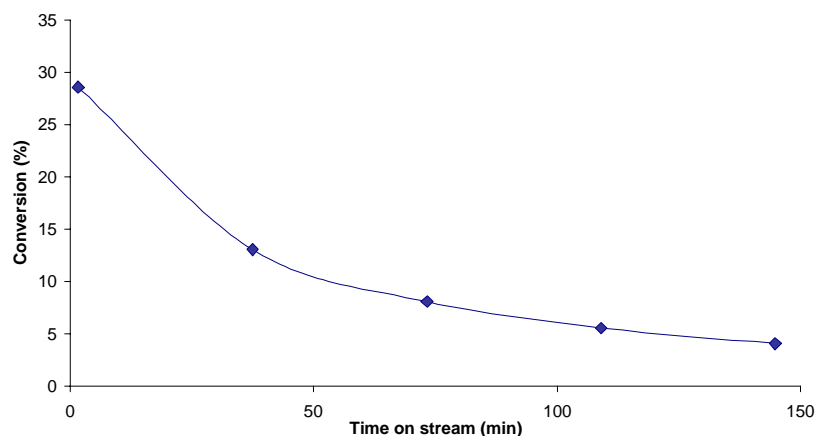
Well-defined silica supported olefin metathesis catalysts

Preparation and characterization



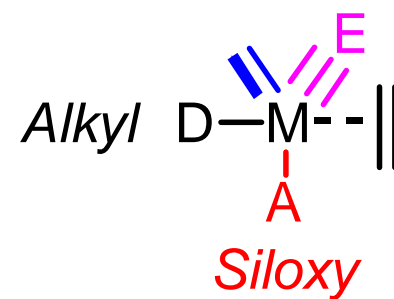
- EXAFS, IR, NMR
& Periodic Calculations

Reactivity (propene metathesis)



- Fast initiation through cross-metathesis
- High initial rates : > 120 mol/mol/min
- Rapid deactivation (6000 TON)
- Formation of 1-butene as a primary product (~2%)

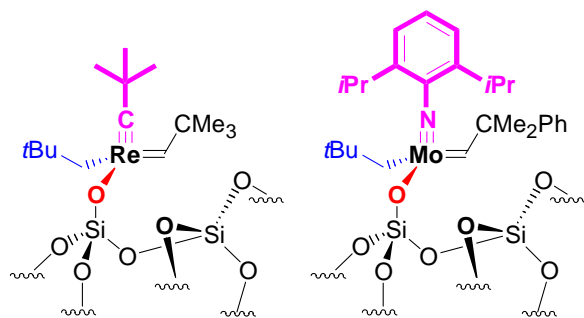
Alkylidene Alkylidyne



M. Chabanas et al. J. Am. Chem. Soc. 2001, 123, 3042.
M. Chabanas et al. J. Am. Chem. Soc. 2003, 125, 492.
X. Solans-Monfort et al. J. Am. Chem. Soc. 2005, 127, 14015.
X. Solans-Monfort et al. New J. Chem. 2006, 30, 842.
 See also poster of X. Solans-Monfort (P12)

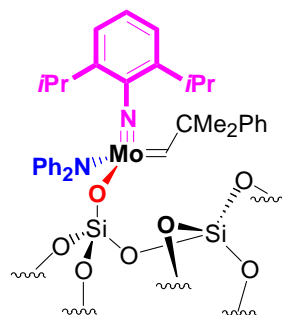
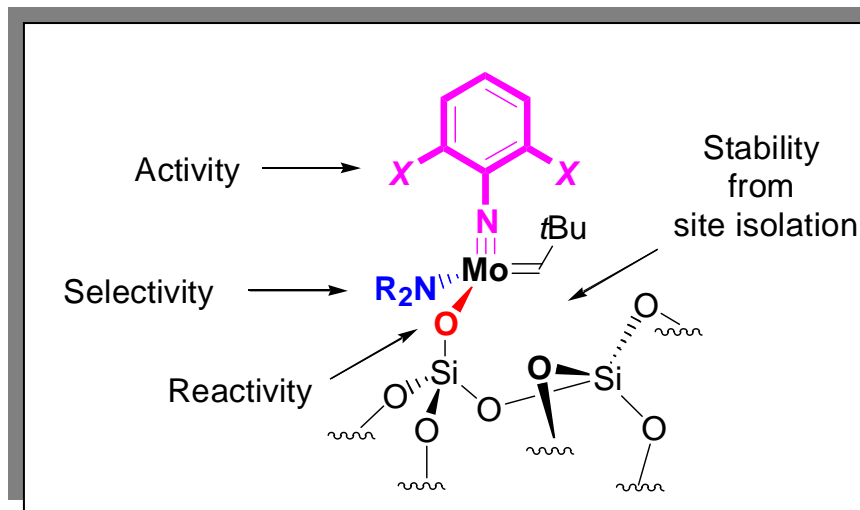
Improvement of catalysts through structure-reactivity relationships

Experimental conditions : propene (Flow reactor)

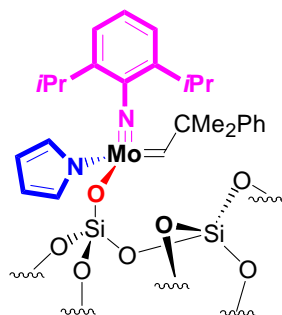


TOF (TON/min) 120
 TON (1500 min) 6000
 Selectivity
 in 2-butenes 96%

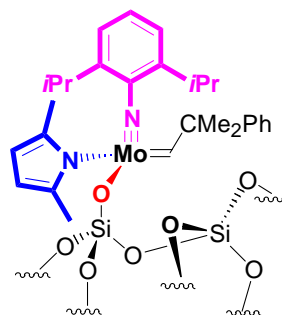
120
 22000
 99.4



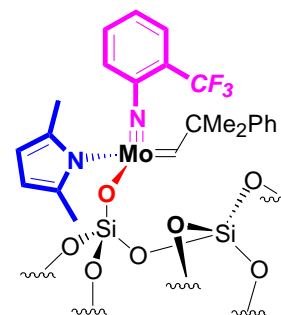
TOF (TON/min) 374
 TON (1500 min) 138000
 Selectivity
 in 2-butenes > 99.9%



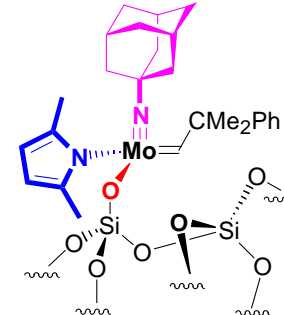
362
 62000
 >99.9%



320
 101000
 > 99.9%



560
 135000
 > 99.9%



780
 275000
 > 99.9%

F. Blanc *et al.* *Angew. Chem. Int. Ed.* **2006**, *123*, 2062.
 F. Blanc *et al.* *J. Am. Chem. Soc.* **2007**, *127*, 1082.
 F. Blanc *et al.* *J. Am. Chem. Soc.* **2007**, *127*, 8434.

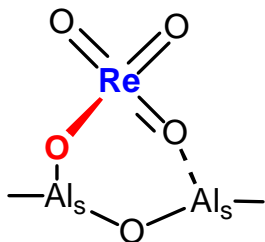
See also,
 F. Blanc: P7 & P23
 X. Solans-Monfort P12

Surface Organometallic Chemistry : Understanding of technical industrial catalysts

Technical Heterogeneous
Catalysis

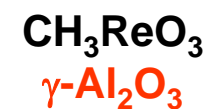
SOMC

Well-defined Heterogeneous
Catalysts



Proposed active site for
 $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$

2% of active site



$\text{MeReO}_3/\text{Nb}_2\text{O}_5$ or $\text{MeReO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$:

Herrmann, W. A. et al. *Angew. Chem.* **1991**, *103*, 1704-1706.

Buffon, R. et al. *J. Mol. Cat.* **1992**, *72*, L7-L10.

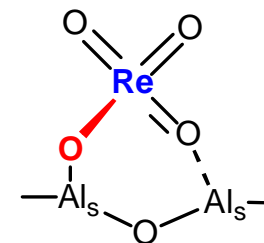
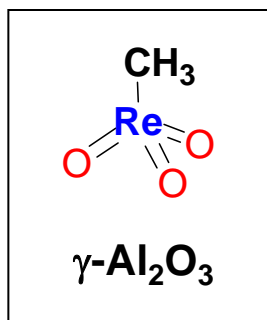
Moses, A. W. et al. *Organometallics* **2006**, *25*, 2157-2165.

Bridging the gap towards technical industrial catalysts

Well-defined Heterogeneous Catalysts

SOMC

Technical Heterogeneous Catalysis



Proposed active site for
 $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$

- Very fast initial activity :
28 TON/min/total Re @ 6 min
- High productivity :
19000 TON/total Re over 2700 min
- Z-selective active sites
- Fast deactivation
- Compatible with functional group
without activators

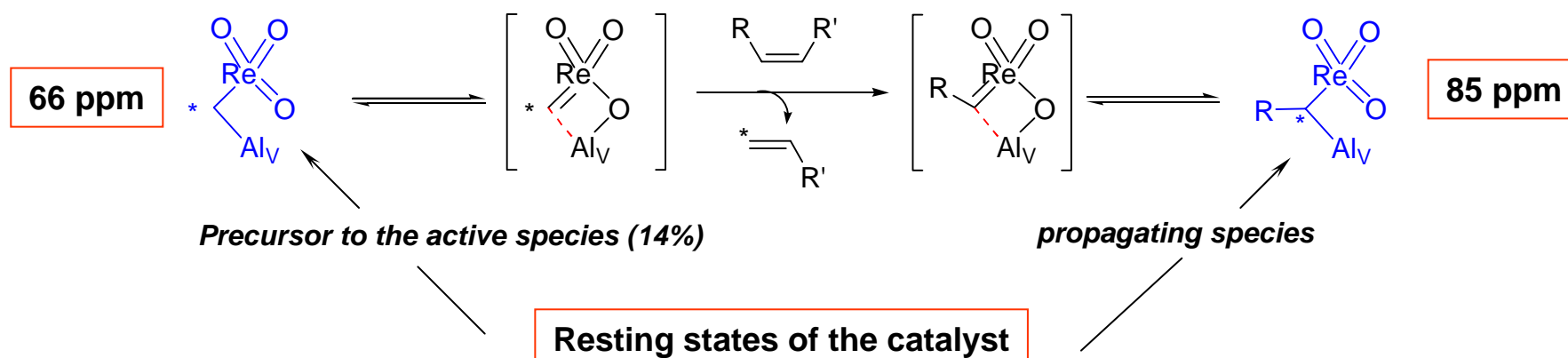
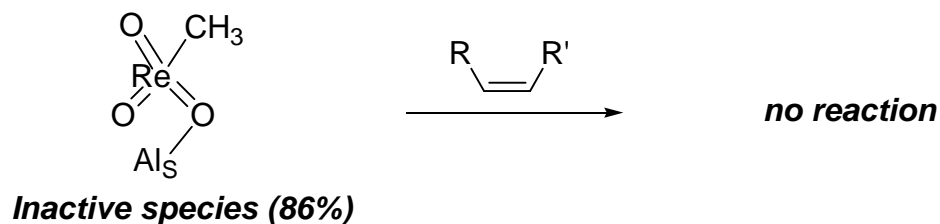
Active sites : unknown

- Slow initial activity :
0.5 TON/min/total Re @ 6 min
- Good productivity :
ca. 1300 TON/total Re over 2700 min
- Z-selective active sites
- Slow deactivation
- Need of co-catalyst (typically Me_4Sn) to
transform functionalized olefins

Active site : 2% (oxo ligands)

What are the active sites in $\text{MeReO}_3/\text{Al}_2\text{O}_3$?
Is the methyl involved or not ?
Can we learn something from $\text{MeReO}_3/\text{Al}_2\text{O}_3$?

Conclusion : structure of the active site(s) of $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_{3-(500)}$



- Highly active in propene metathesis
(Initial rate = 28 TON/min/Re)
- Active in the metathesis of functional olefins (without any promoter)
- Very fast deactivation
- 14-15% of active sites
 TOF ~ 188 TON/min/active site
 TON ~ 17000 /active Re