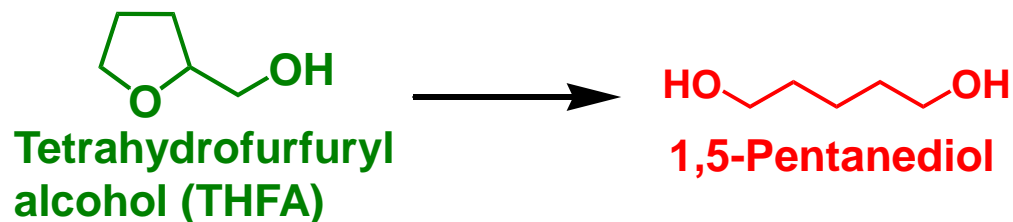


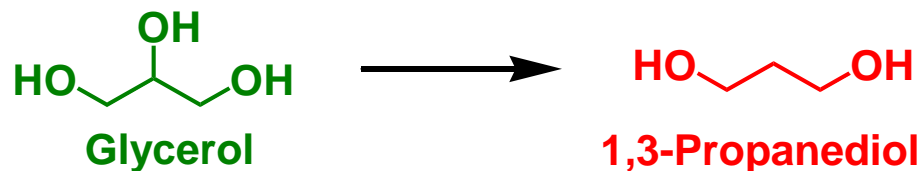
## 金属-酸化物界面を活性点とするC-O結合水素化分解反応 東北大院工 富重圭一

1. C-O結合水素化分解反応とバイオマス化学品製造
2. Rh-ReO<sub>x</sub>及びRh-MoO<sub>x</sub>触媒を用いたテトラヒドロフルフリルアルコールの水素化分解



3. Ir-ReO<sub>x</sub>触媒を用いたグリセリンの水素化分解

4. Ir-ReO<sub>x</sub>構造解析



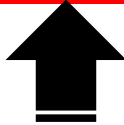
# 資源とターゲット化学品の組成

**バイオマス**  
(酸素含有率が高い)



還元(水素)

**ターゲット**  
 $\text{HO}(\text{CH}_2)_n\text{OH}$



酸化  
水和

**石油**  
(酸素を含まない)

**新しい触媒反応と  
それを実現する触媒  
のニーズ**

**C-O結合水素化分解が重要**



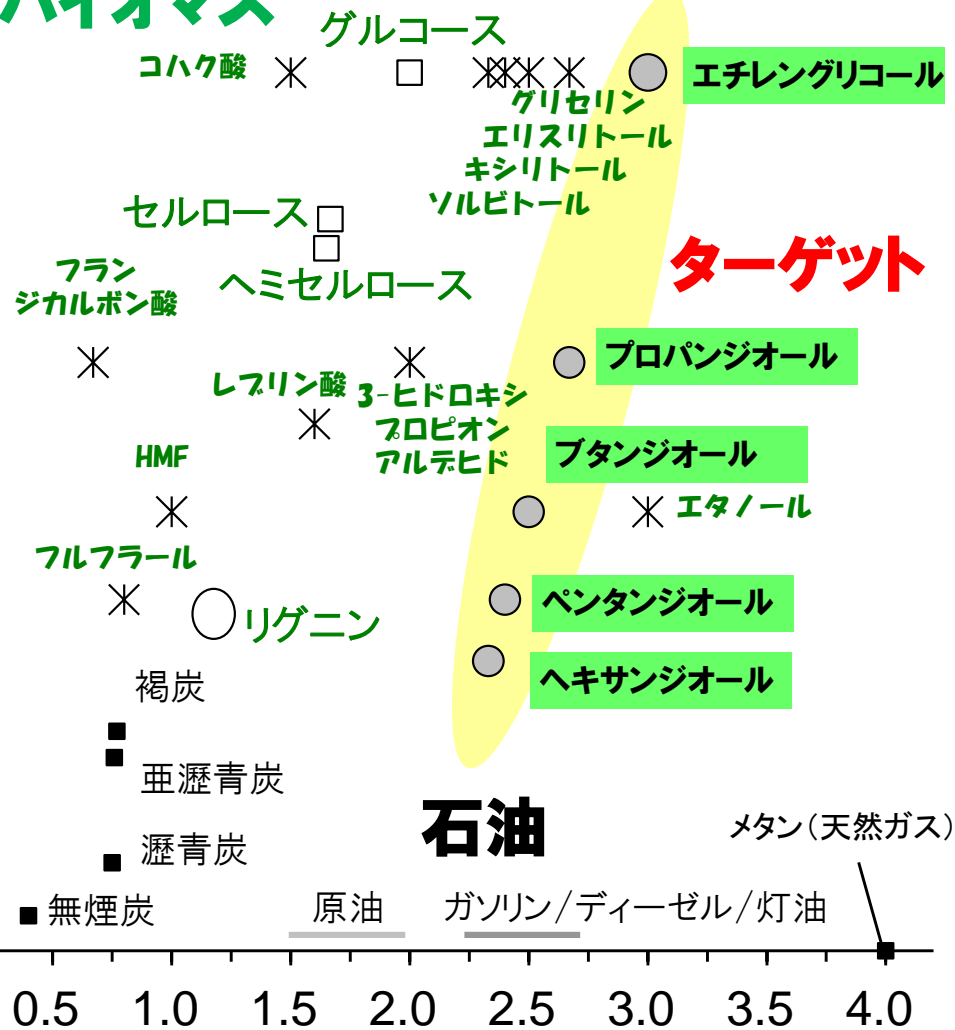
O/C (mol/mol)

1.0  
0.8  
0.6  
0.4  
0.2  
0.0

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

H/C (mol/mol)

**バイオマス**

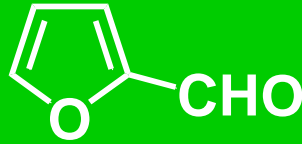


**本触媒は化学品製造の  
原料転換のための重要技術**

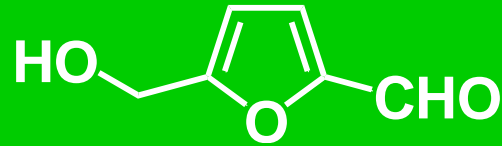
# バイオマスの発酵、脱水などにより得られる基幹原料



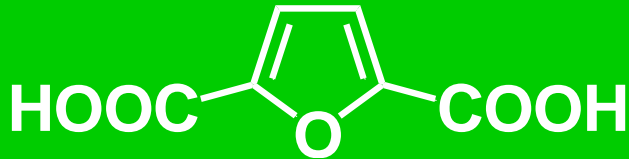
Ethanol



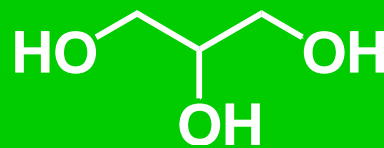
Furfural



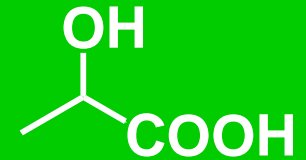
Hydroxymethylfurfural



Furan-2,5-dicarboxylic acid



Glycerol



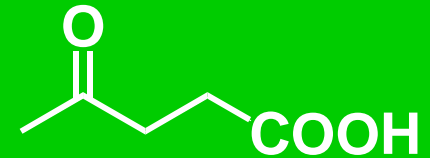
Lactic acid



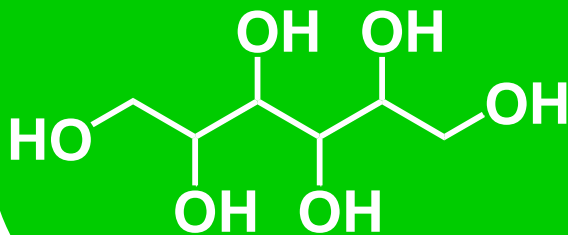
Succinic acid



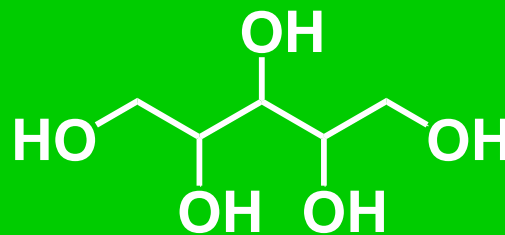
3-Hydroxypropionaldehyde



Levulinic acid



Sorbitol

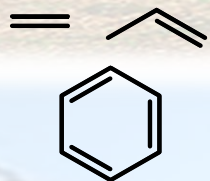


Xylitol

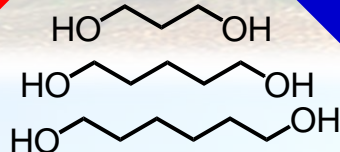
G.R. Petersen et al.,  
Green Chem., 2010

# バイオマス化学品合成の化学 鍵となる3つの視点

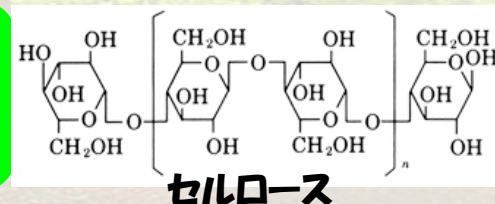
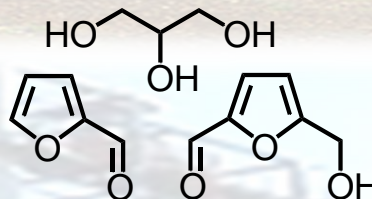
石油  
=化石資源  
(炭化水素)



繊維、樹脂原料  
(ナイロン)  
(ポリエステル)  
(ポリウレタン)



バイオマス  
=再生可能資源  
(含酸素化合物)



## 1. バイオマス化学品合成は還元反応

石油由来炭化水素は空気酸化。バイオマスは、水素で還元。  
空気は安価。水素は高価。→リニューアブルな水素製造は重要。

還元反応  
水素  
(触媒)

## 2. バイオマス化学品合成は液相反応

石油由来炭化水素は低極性・低沸点。→気相反応が可能(気・固相)  
バイオマス由来化合物は高極性・高沸点。→液相反応。溶媒に配慮が必要。

極性溶媒  
極性反応場

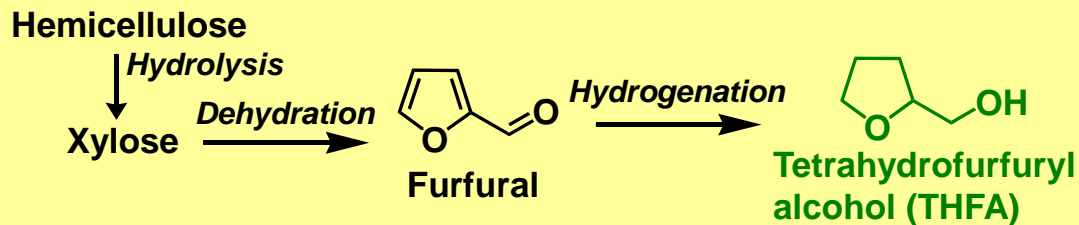
## 3. バイオマス化学品合成は官能基認識が不可欠

石油由来炭化水素は官能基付加反応。バイオマス由来化合物は、官能基を減らす反応。どの官能基を取り除くかの認識が必要。

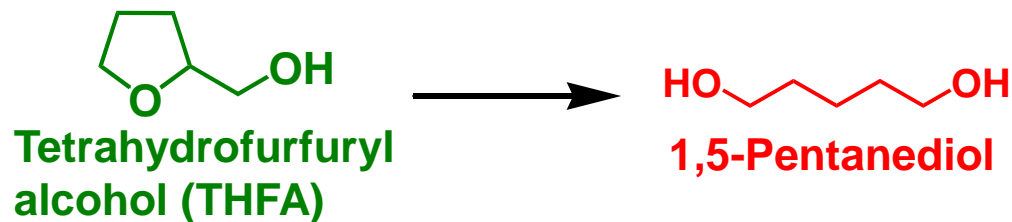
官能基認識  
(触媒)

グリーンサステナブルケミストリー研究会(第4回) 2015/12/8  
触媒研究の近未来 -作用中の触媒に迫る-  
SPring-8利用推進協議会 研究開発委員会

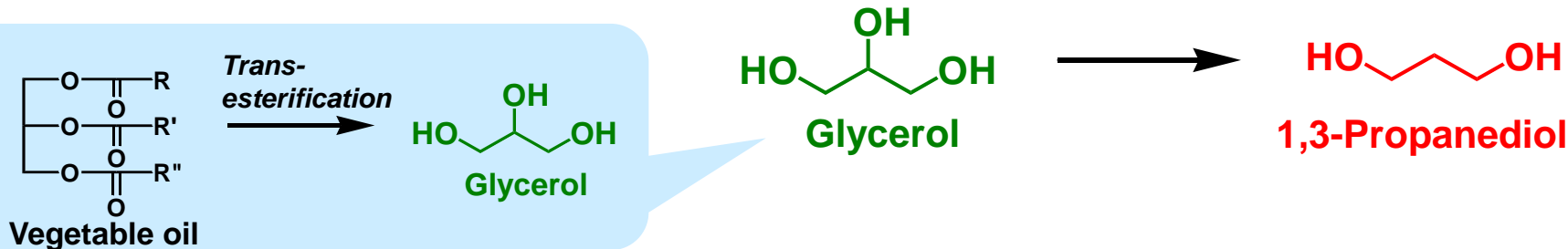
金属-酸化物界面を介した触媒作用



1. C-O結合水素化分解反応とバイオマス化学品製造
2. Rh-ReO<sub>x</sub>及びRh-MoO<sub>x</sub>触媒を用いたテトラヒドロフルフリルアルコールの水素化分解



3. Ir-ReO<sub>x</sub>触媒を用いたグリセリンの水素化分解



# 新しい炭素—酸素結合水素化分解反应用 触媒の構造 (Ir-ReO<sub>x</sub>, Rh-ReO<sub>x</sub>, Rh-MoO<sub>x</sub>)

XRD, TEM,  
昇温水素還元, XPS,  
CO吸着量測定,  
CO吸着FTIR,  
XAFS, XANES

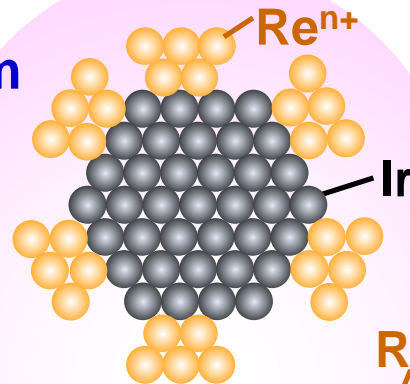
## ReO<sub>x</sub> 3-D clusters on Ir metal particles (2 nm)

(J. Phys. Chem. C, 116, 23503 (2012))

Re-O: 1.6, 0.204 nm

Re-Ir (or -Re) : 5.5, 0.265 nm

(最適比Re/Ir=1)



## ReO<sub>x</sub> 2-D clusters on Rh metal particles (3 nm)

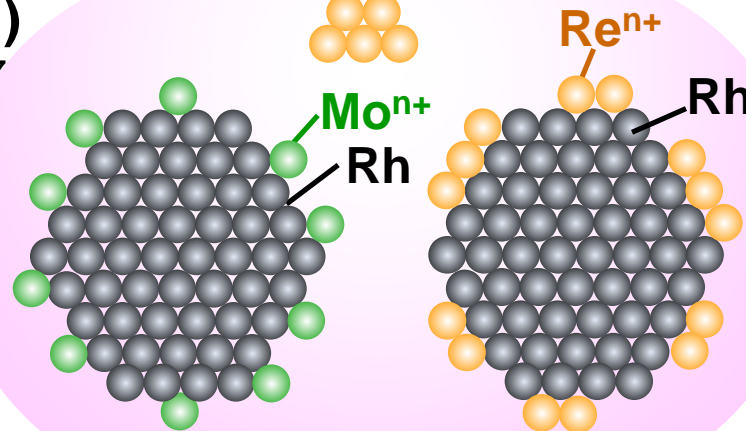
(J. Phys. Chem. C, 116, 3079 (2012))

(最適比Re/Rh=0.5)

Re-O: 1.5, 0.209 nm

Re-Rh: 3.3, 0.265 nm

Re-Re: 2.7, 0.270 nm



## Isolated MoO<sub>x</sub> on Rh metal particles (3 nm)

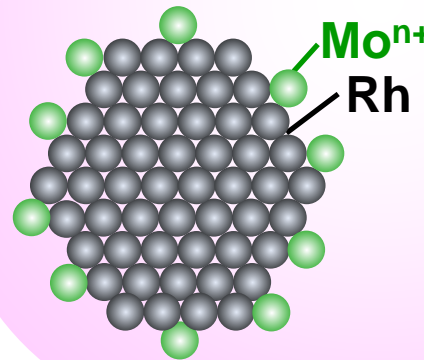
(Appl. Catal. B, 111-112, 27 (2012))

(最適比Mo/Rh=0.13)

Mo-O: 1.1, 0.208 nm

Mo-Rh (or -Mo):

3.0, 0.264 nm



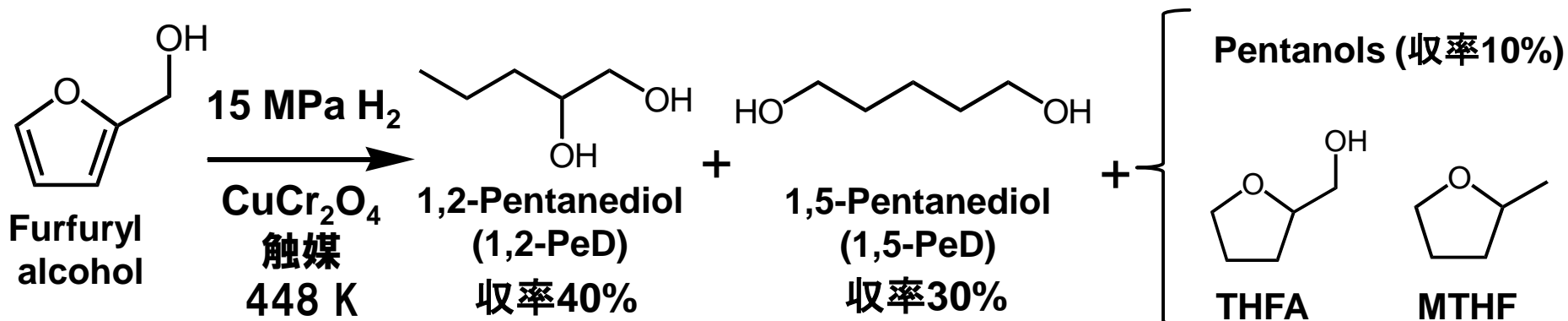
金属酸化物修飾(Re, Mo)-  
金属微粒子(Ir, Rh)触媒

吸収原子—  
散乱原子

配位数,  
結合距離

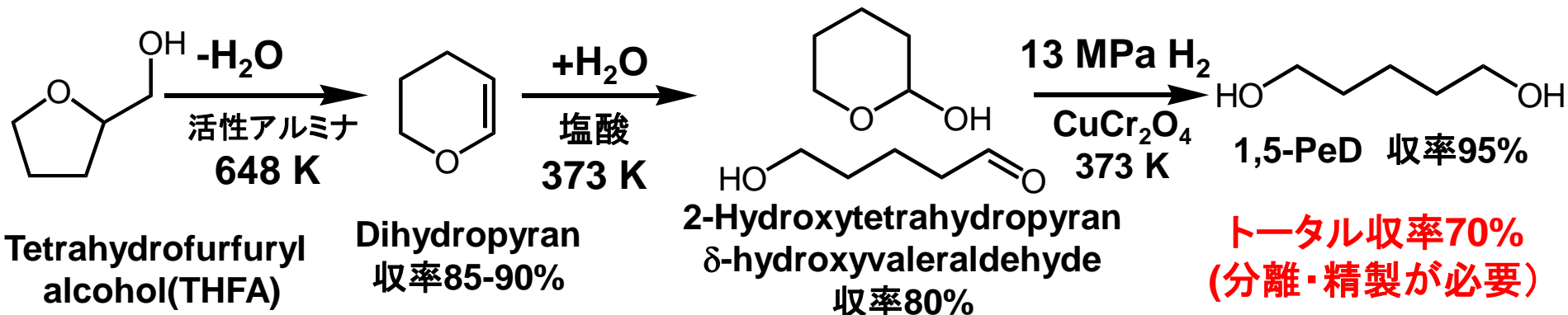
# 1, 5-ペンタンジオール合成に関する先行研究

## 1) 従来型水素化分解触媒 $\text{CuCr}_2\text{O}_4$ の使用：非選択的



H. Adkins, et al., J. Am. Chem.Soc. 53 (1931) 1091

## 2) 3段階反応（それぞれの段階では純粋な試薬を使用）

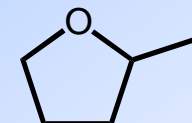
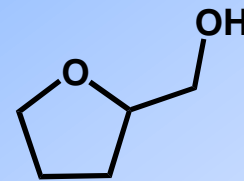


L. E. Schniepp, et al., J. Am. Chem.Soc. 68 (1948) 1646

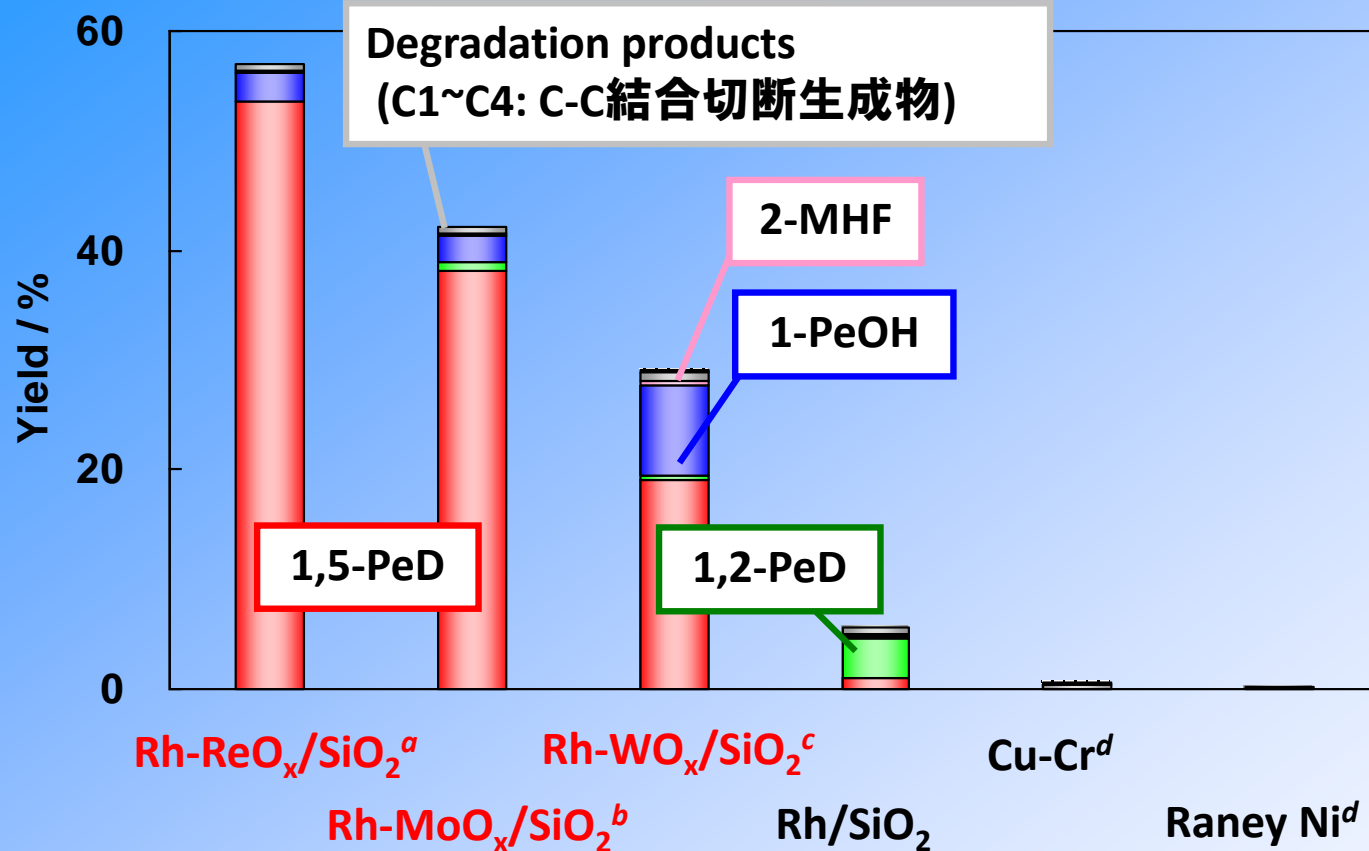
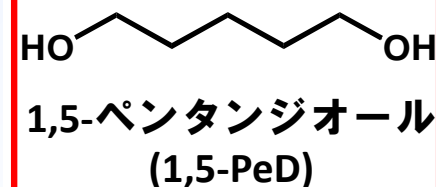
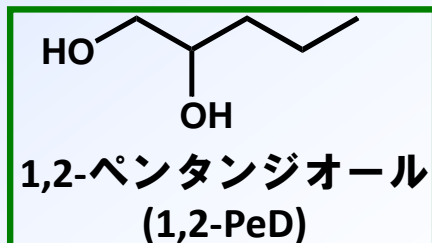
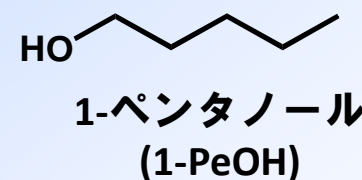
“直接水素化分解による1,5-ペンタンジオール合成が望まれる  
(おそらく均一系触媒が使われるだろう)。”

M. Schlaf, Dalton Trans. 4645 (2006)

# テトラヒドロフルフリルアルコール (THFA) の水素化分解反応



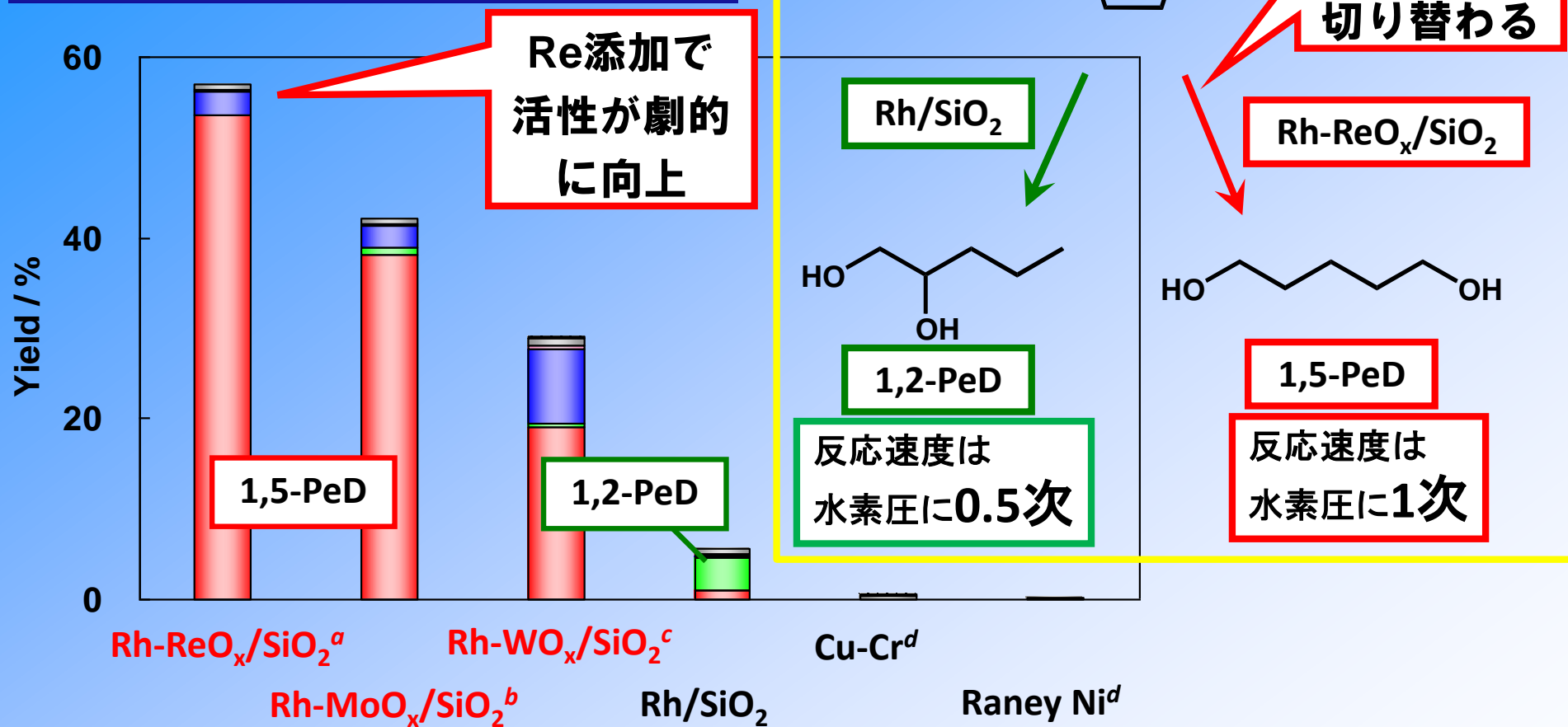
2-メチル  
テトラヒドロフラン  
(2-MHF)



Conditions :  $P = 8.0 \text{ MPa}$ ,  $T = 393 \text{ K}$ ,  $t = 4 \text{ h}$ ,  $m_{cat} = 50 \text{ mg}$ ,  
 Reactant = 5 wt% THFA aq. 20 ml,  
 Rh: 4 wt%, <sup>a</sup>Re/Rh=0.5, <sup>b</sup>Mo/Rh=0.125,  
<sup>c</sup>W/Rh=0.125, <sup>d</sup> $T = 453 \text{ K}$ ,  $m_{cat} = 500 \text{ mg}$ .



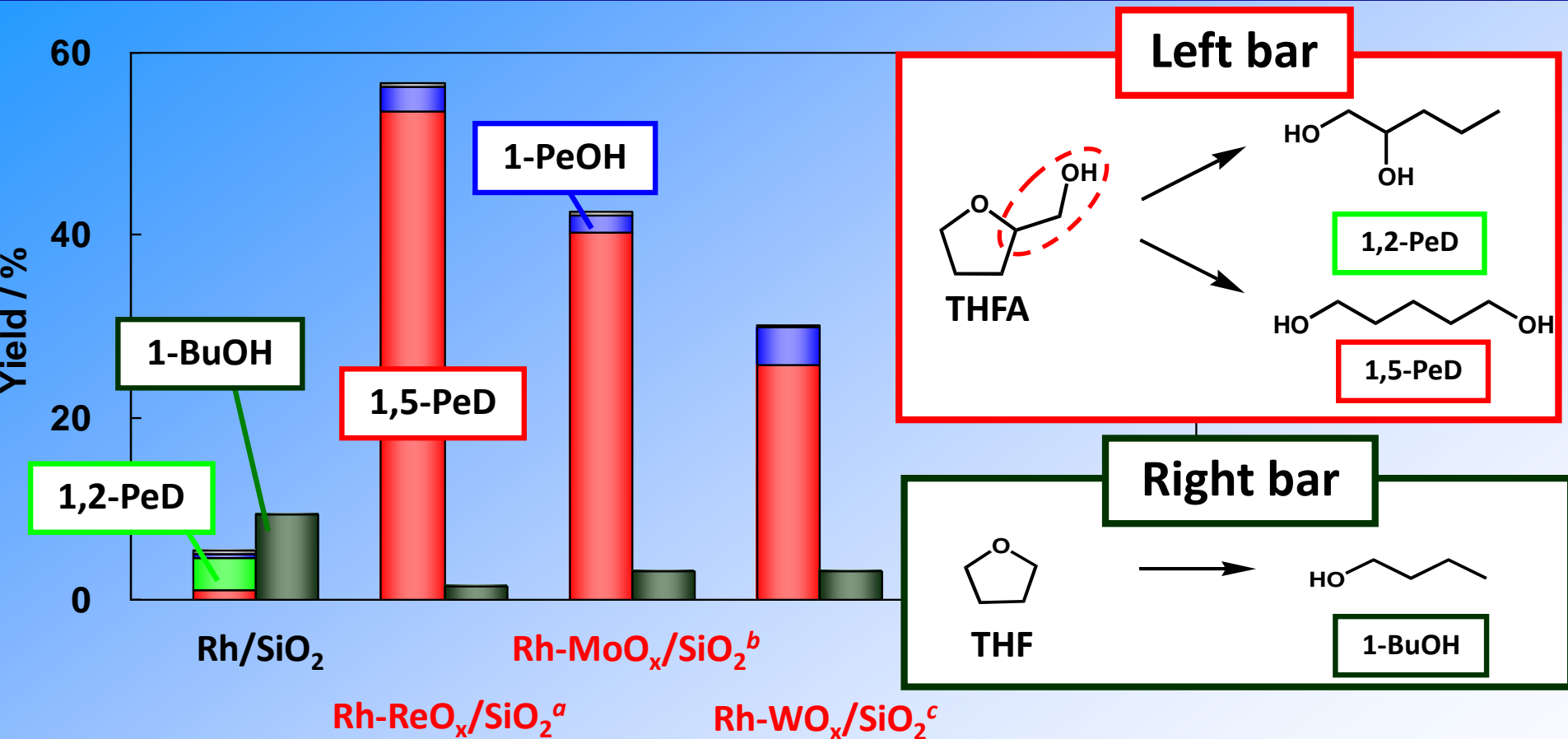
# THFAの水素化分解反応



活性: Rh-MO<sub>x</sub>/SiO<sub>2</sub> (M = Re, Mo, W) > Rh/SiO<sub>2</sub> >> 従来触媒

高選択的に1,5-PeD合成

# THFAとテトラヒドロフラン(THF)の水素化分解反応比較



Conditions :

$P = 8.0 \text{ MPa}$ ,  $T = 393 \text{ K}$ ,  $t = 4 \text{ h}$ ,  $m_{cat} = 50 \text{ mg}$ ,

Reactant = 5 wt% THFA aq. 20 ml, 5 wt% THF aq. 20 ml

Rh: 4 wt%, <sup>a</sup>Re/Rh=0.5, <sup>b</sup>Mo/Rh=0.125, <sup>c</sup>W/Rh=0.125

Chem. Commun. 2035, 61 (2009)

J. Catal. 267, 89 (2009)

THFA活性 : Rh/SiO<sub>2</sub> << Rh-MO<sub>x</sub>/SiO<sub>2</sub>

THF活性 : Rh-MO<sub>x</sub>/SiO<sub>2</sub> < Rh/SiO<sub>2</sub>

活性序列  
逆転

高選択的に  
1,5-PeD合成  
のカギ

-CH<sub>2</sub>OH基  
の存在で反  
応性向上

# 使用触媒・実験

## 使用触媒 (逐次含浸法にて調製)

- Rh/SiO<sub>2</sub>                   ... Rh: 4 wt%
- Rh-ReO<sub>x</sub>/SiO<sub>2</sub>           ... Rh: 4 wt%, Re/Rh = 0.13, 0.25, 0.5, 1
- Rh-MoO<sub>x</sub>/SiO<sub>2</sub>           ... Rh: 4 wt%, Mo/Rh = 0.03, 0.06, 0.13, 0.25, 0.5

(\*) 担体: SiO<sub>2</sub>:富士シリシア製G-6 (BET表面積535 m<sup>2</sup>·g<sup>-1</sup>)

[ Rh: RhCl<sub>3</sub>·3H<sub>2</sub>O, Re: NH<sub>4</sub>ReO<sub>4</sub>, Mo: (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O ]

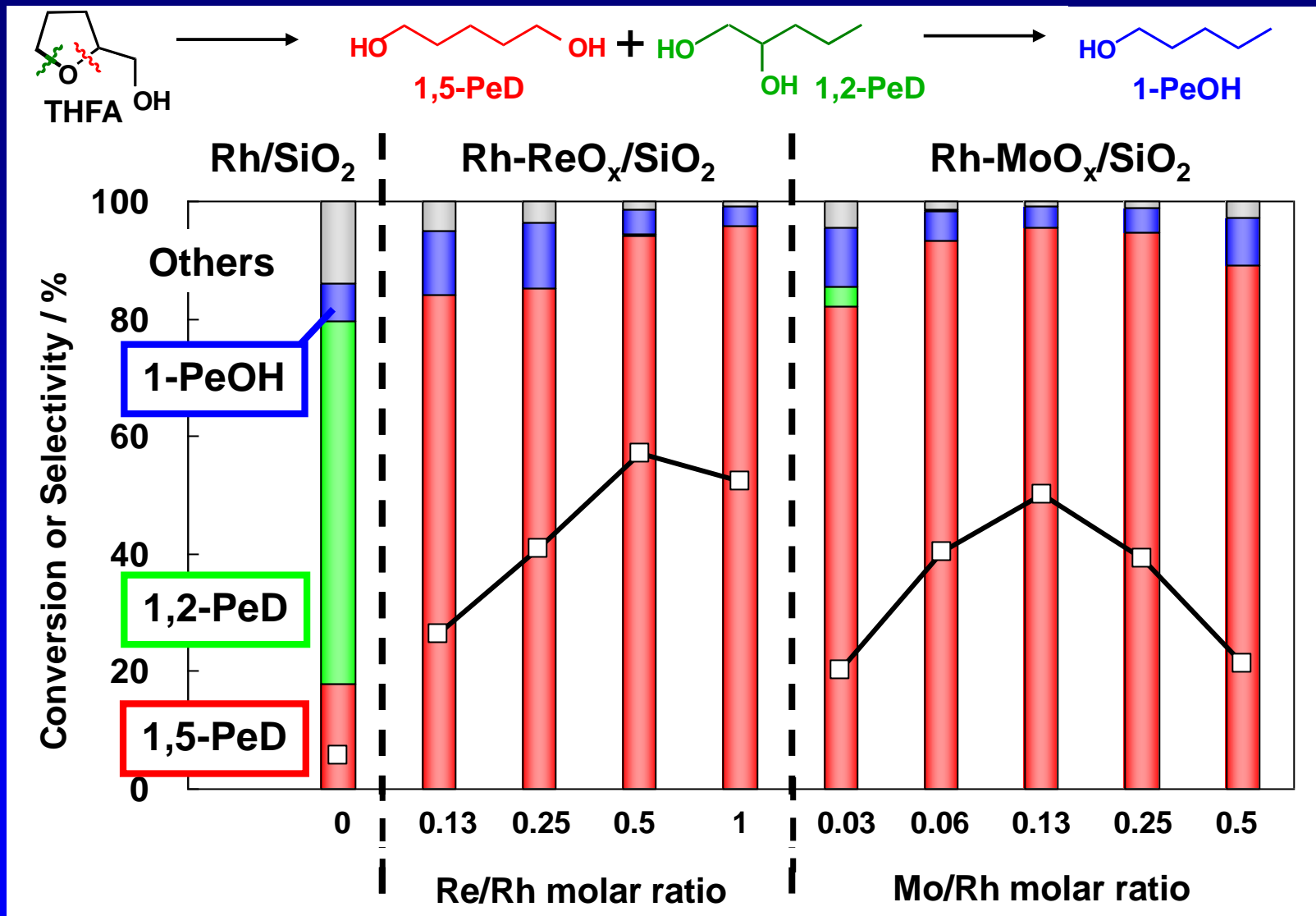
## 活性試験 (Re, Mo添加量依存実験)

○回分式反応装置 (オートクレーブ)

## キャラクタリゼーション

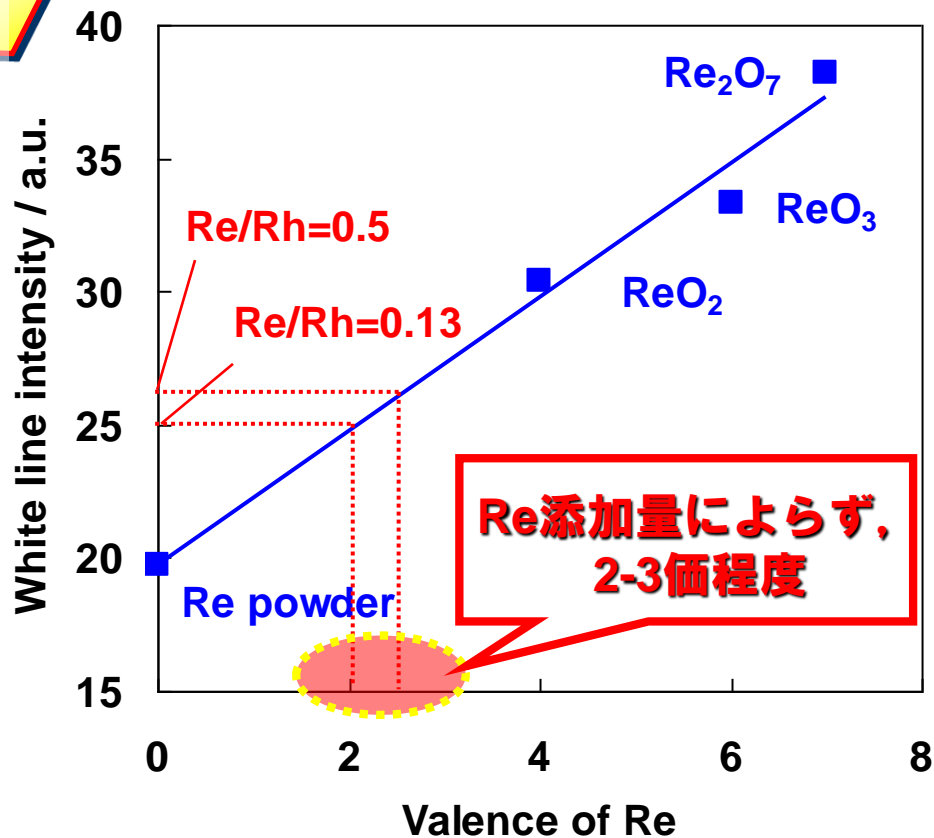
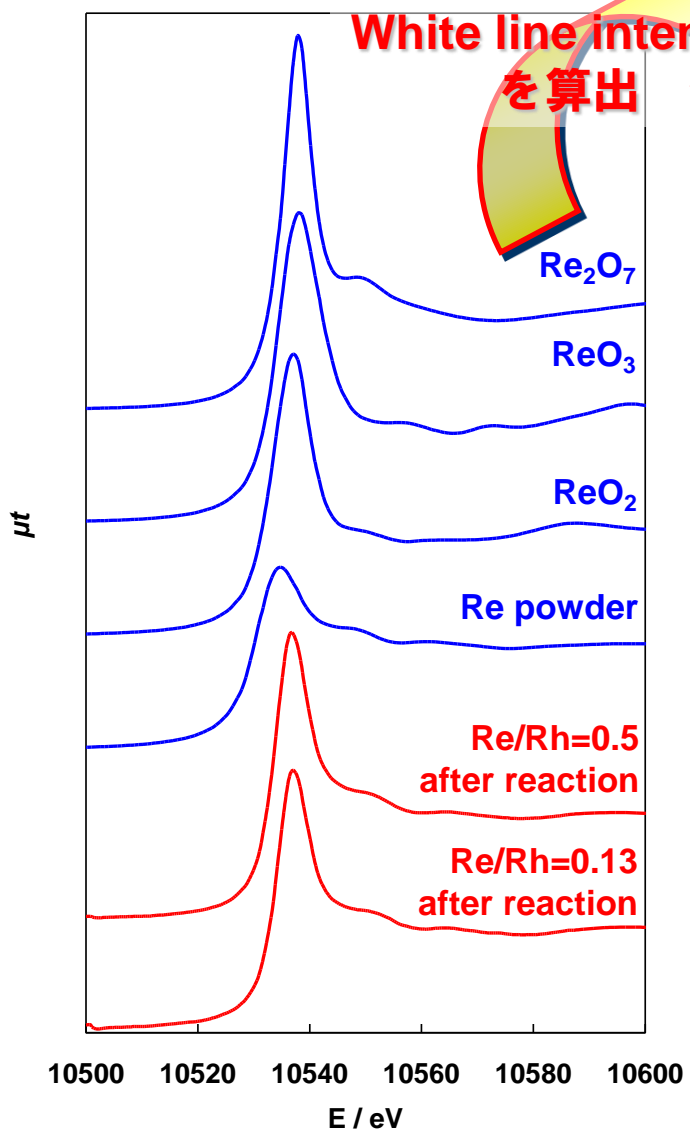
- CO吸着                   ... 表面Rh金属数
- XRD, TEM               ... 金属微粒子の平均粒子径
- Re L<sub>3</sub>-edge XANES      ... Reの価数
- Re L<sub>3</sub>-edge, Mo K-edge EXAFS   ... Re, Mo周りの触媒構造

# Re, Mo添加量依存



Conditions :  $P = 8.0$  MPa,  $T = 393$  K,  $m_{cat} = 50$  mg,  $t = 4$  h,  
 Rh = 4 wt%, Reactant = 5 wt% THFA aqueous solution 20 ml.

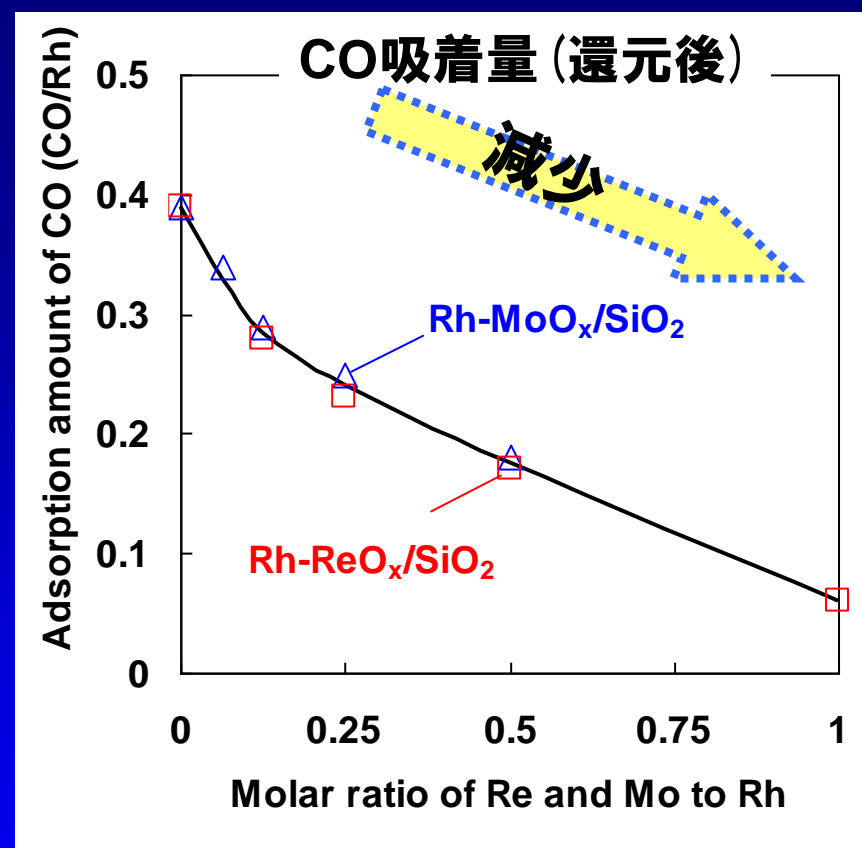
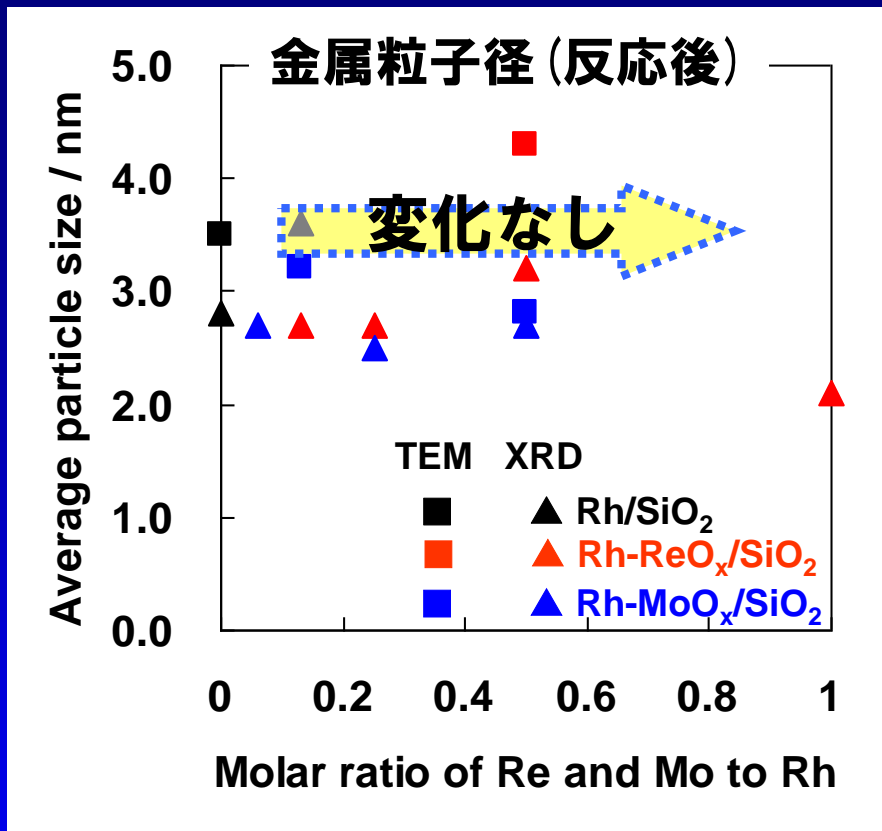
# Re $L_3$ -edge XANES



反応中のReは酸化物状態で存在

⇒ TPRの結果と合致

# 金属粒子径・CO吸着量測定



**金属粒子径変化なし**

**Re, Mo添加⇒CO吸着量減少, 傾向類似**  
**Re, Moは酸化物⇒CO吸着しない**

**ReまたはMo酸化物がRh金属微粒子表面を部分的に覆う**

# Characterization of Rh-MO<sub>x</sub>/SiO<sub>2</sub> (M: Re, Mo)

Appl. Catal. B, in press

| Catalyst                              | Mo/Rh<br>or Re/Rh | Particle size<br>XRD (nm) | Dispersion <sup>a</sup>   |       | CO adsorption (Rh <sub>s</sub> /Rh) |  |
|---------------------------------------|-------------------|---------------------------|---------------------------|-------|-------------------------------------|--|
|                                       |                   |                           | XRD [Rh <sub>s</sub> /Rh] | CO/Rh | -(CO/Rh)                            |  |
| Rh/SiO <sub>2</sub>                   | -                 | 2.8                       | 0.39                      | 0.39  | 0.0                                 |  |
| Rh-MoO <sub>x</sub> /SiO <sub>2</sub> | 0.06              | 2.7                       | 0.41                      | 0.34  | 0.07                                |  |
|                                       | 0.13              | 2.6                       | 0.42                      | 0.29  | 0.13                                |  |
|                                       | 0.25              | 2.5                       | 0.44                      | 0.25  | 0.19                                |  |
|                                       | 0.5               | 2.7                       | 0.41                      | 0.18  | 0.23                                |  |
| Rh-ReO <sub>x</sub> /SiO <sub>2</sub> | 0.13              | 2.7                       | 0.41                      | 0.28  | 0.13                                |  |
|                                       | 0.25              | 2.7                       | 0.41                      | 0.23  | 0.18                                |  |
|                                       | 0.5               | 3.2                       | 0.34                      | 0.17  | 0.17                                |  |

<sup>a</sup> Rh<sub>s</sub>/Rh=1.098 nm/particle size

(Rh<sub>s</sub>/Rh)-(CO/Rh): MoO<sub>x</sub> and ReO<sub>x</sub> でおおわれるRh表面の割合  
 Mo/Rh, Re/Rh ≤ 0.13: Mo or Re 原子一つが一つのCO吸着量を抑制  
 Mo/Rh=Re/Rh > 0.13: 一部のMo or Reの原子はCO吸着を抑制しない

# Characterization CO adsorption

Rh金属の粒子径及び分散度はほぼ一定

(M: Re, Mo)

Appl. Catal. B, in press

| Catalyst                              | Mo/Rh<br>or Re/Rh | Particle size<br>XRD (nm) | Dispersion <sup>a</sup><br>D [Rh <sub>s</sub> /Rh] | CO adsorption<br>CO/Rh | (Rh <sub>s</sub> /Rh)<br>-(CO/Rh) |
|---------------------------------------|-------------------|---------------------------|--|------------------------|-----------------------------------|
| Rh/SiO <sub>2</sub>                   | -                 | 2.8                       | 0.39   | 0.39                   | 0.0                               |
| Rh-MoO <sub>x</sub> /SiO <sub>2</sub> | 0.06              | 2.7                       | 0.41   | 0.34                   | 0.07                              |
|                                       | 0.13              | 2.6                       | 0.42   | 0.29                   | 0.13                              |
|                                       | 0.25              | 2.5                       | 0.44   | 0.25                   | 0.19                              |
|                                       | 0.5               | 2.7                       | 0.41   | 0.18                   | 0.23                              |
| Rh-ReO <sub>x</sub> /SiO <sub>2</sub> | 0.13              | 2.6                       | 0.42   | 0.28                   | 0.13                              |
|                                       | 0.25              | 2.5                       | 0.44   | 0.23                   | 0.18                              |
|                                       | 0.5               | 2.7                       | 0.41   | 0.17                   | 0.17                              |

添加量とともにCO吸着量は減少

<sup>a</sup> Rh<sub>s</sub>/Rh=1.098 nm/particle size

(Rh<sub>s</sub>/Rh)-(CO/Rh): MoO<sub>x</sub> and ReO<sub>x</sub> でおおわれるRh表面の割合  
 Mo/Rh, Re/Rh ≤ 0.13: Mo or Re 原子一つが一つのCO吸着量を抑制  
 Mo/Rh=Re/Rh > 0.13: 一部のMo or Reの原子はCO吸着を抑制しない



# Characterization CO adsorption

Rh金属の粒子径及び分散度はほぼ一定

(M: Re, Mo)

Appl. Catal. B, in press

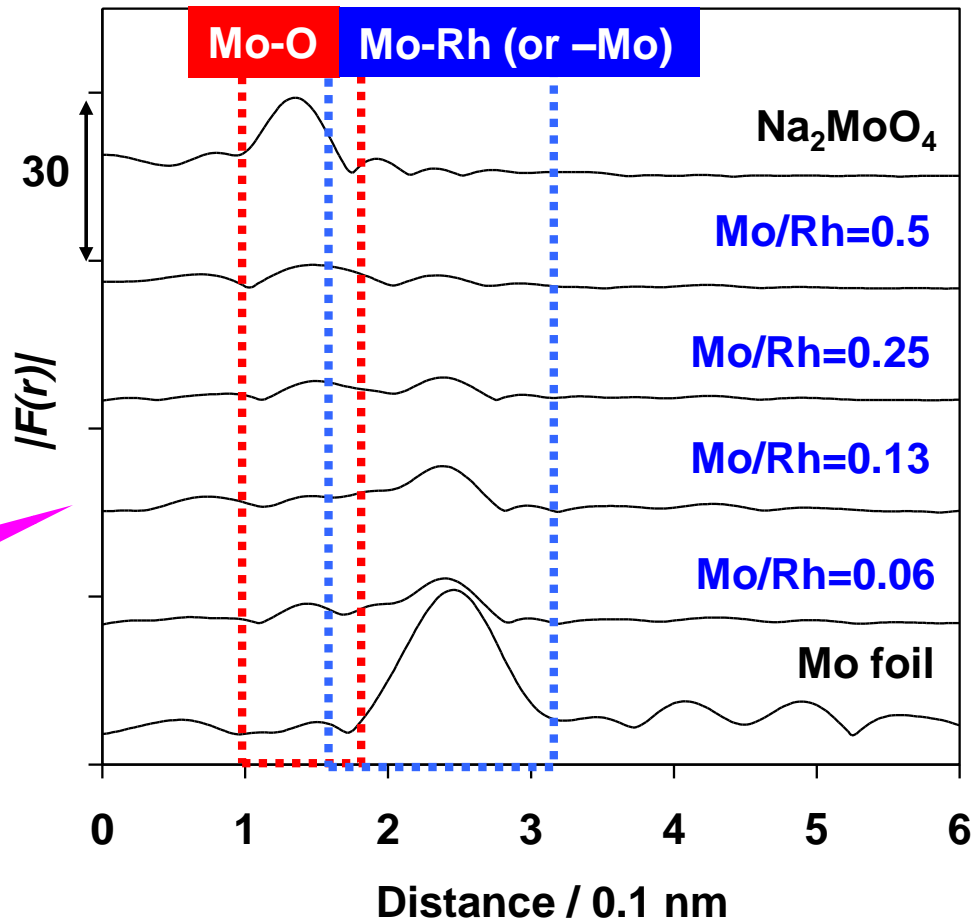
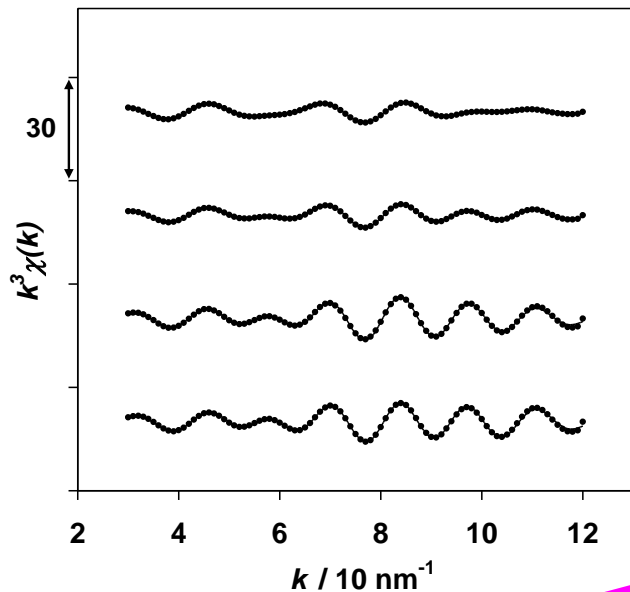
| Catalyst                              | Mo/Rh<br>or Re/Rh | Particle size<br>XRD (nm) | Dispersion <sup>a</sup><br>D [Rh <sub>s</sub> /Rh] | CO adsorption<br>CO/Rh | (Rh <sub>s</sub> /Rh)<br>-(CO/Rh) |
|---------------------------------------|-------------------|---------------------------|--|------------------------|-----------------------------------|
| Rh/SiO <sub>2</sub>                   | -                 | 2.8                       | 0.39   | 0.39                   | 0.0                               |
| Rh-MoO <sub>x</sub> /SiO <sub>2</sub> | 0.06              | 2.7                       | 0.41   | 0.34                   | 0.07                              |
|                                       | 0.13              | 2.6                       | 0.42   | 0.29                   | 0.13                              |
|                                       | 0.25              | 2.5                       | 0.44   | 0.25                   | 0.19                              |
|                                       | 0.5               | 2.7                       | 0.41   | 0.18                   | 0.23                              |
| Rh-ReO <sub>x</sub> /SiO <sub>2</sub> | 0.13              | 2.6                       | 0.42   | 0.28                   | 0.13                              |
|                                       | 0.25              | 2.5                       | 0.44   | 0.23                   | 0.18                              |
|                                       | 0.5               | 2.7                       | 0.41   | 0.17                   | 0.17                              |

添加量とともにCO吸着量は減少

<sup>a</sup> Rh<sub>s</sub>/Rh=1.098 nm/particle size

Mo/Rh=Re/Rh = 0.13では、添加したMo or ReがすべてCO吸着を抑制  
 添加したMo or ReがすべてRh金属表面と相互作用  
 → Mo/Rh=Re/Rh = 0.13 の構造解析(EXAFS)

# Characterization of Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo K-edge EXAFS)



## Curve fitting analysis

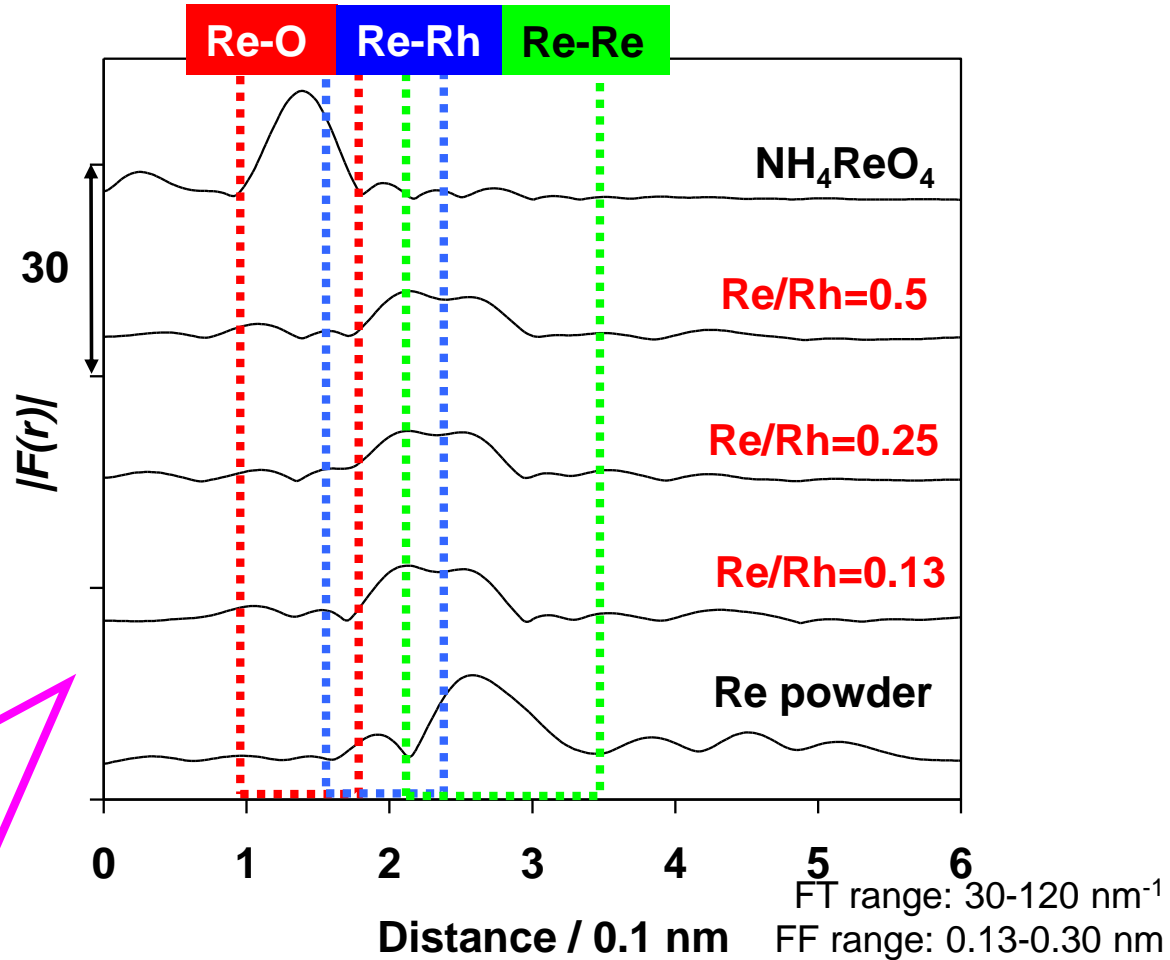
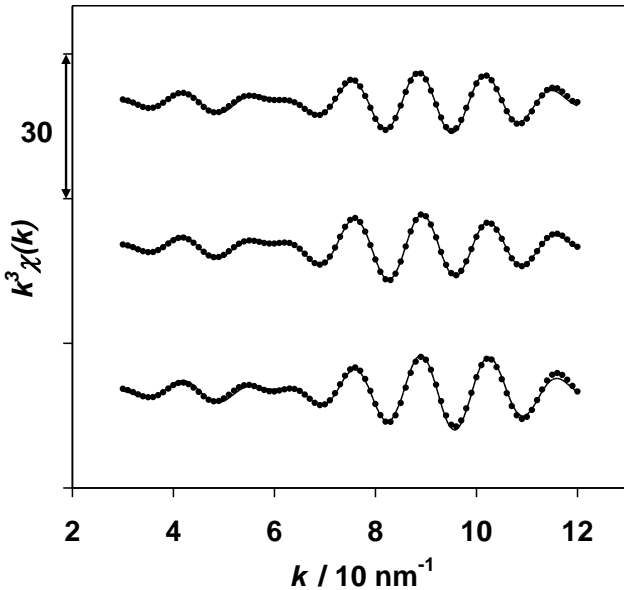
| Mo/Rh | Shells         | CN <sup>a</sup> | R / nm <sup>b</sup> |
|-------|----------------|-----------------|---------------------|
| 0.5   | Mo-O           | 2.6             | 0.204               |
|       | Mo-Rh (or -Mo) | 1.4             | 0.262               |
| 0.25  | Mo-O           | 1.7             | 0.203               |
|       | Mo-Rh (or -Mo) | 2.3             | 0.264               |
| 0.13  | Mo-O           | 1.1             | 0.208               |
|       | Mo-Rh (or -Mo) | 3.0             | 0.264               |
| 0.06  | Mo-O           | 0.9             | 0.201               |
|       | Mo-Rh (or -Mo) | 3.5             | 0.265               |

FT range: 30-120 nm<sup>-1</sup>, FF range: 0.13-0.28 nm

**MoとRhは直接相互作用  
(配位数3程度)**

<sup>a</sup> Coordination number. <sup>b</sup> Bond distance.

# Characterization of Rh-ReO<sub>x</sub>/SiO<sub>2</sub> (Re L<sub>3</sub>-edge EXAFS)



## Curve fitting analysis

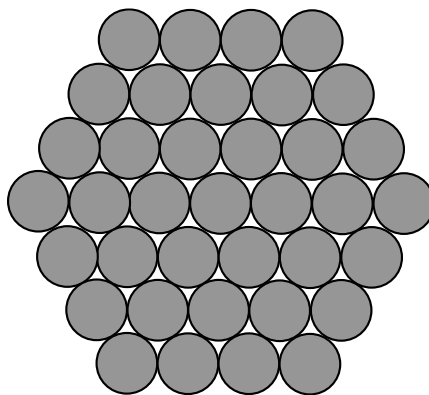
| Re/Rh | Shells | CN <sup>a</sup> | R / nm <sup>b</sup> |
|-------|--------|-----------------|---------------------|
| 0.5   | Re-O   | 1.3             | 0.213               |
|       | Re-Rh  | 3.6             | 0.268               |
|       | Re-Re  | 2.8             | 0.273               |
| 0.25  | Re-O   | 1.2             | 0.210               |
|       | Re-Rh  | 3.6             | 0.267               |
|       | Re-Re  | 2.2             | 0.273               |
| 0.13  | Re-O   | 0.6             | 0.213               |
|       | Re-Rh  | 3.8             | 0.266               |
|       | Re-Re  | 2.0             | 0.271               |

**ReとRhは直接相互作用(配位数~3)**  
**Re-Re結合も観測→クラスター状**

<sup>a</sup> Coordination number. <sup>b</sup> Bond distance.

Model structure of Rh-MO<sub>x</sub>/SiO<sub>2</sub> (M: Re, Mo; M/Rh=0.13)

Top view

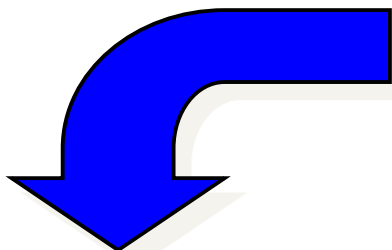


Rh metal surface  
(1 1 1)

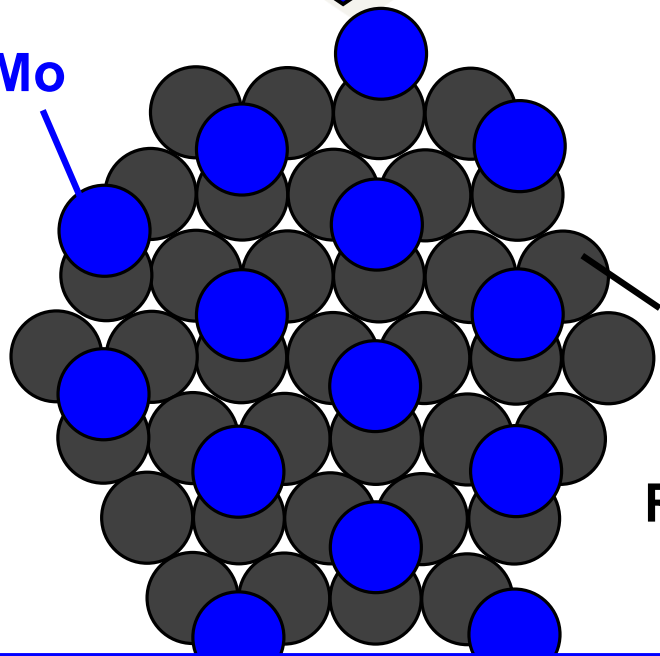
Rh with adjoining  
Mo or Re

Rh without adjoining Re

Mo/Rh=0.13

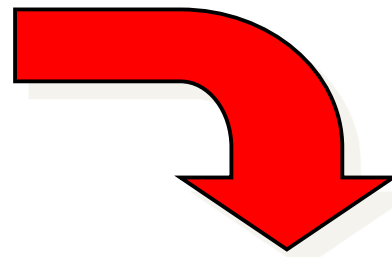


Mo

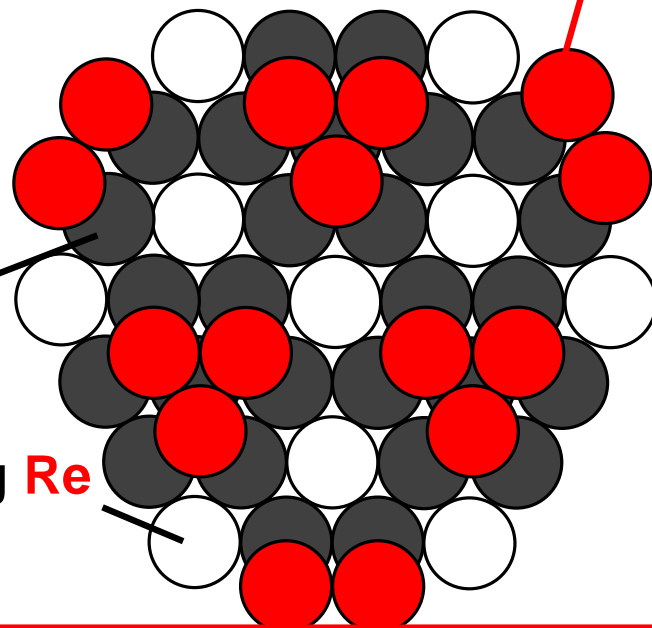


孤立 MoO<sub>x</sub> 種がRh表面の3-fold hollowサイトに

Re/Rh=0.13

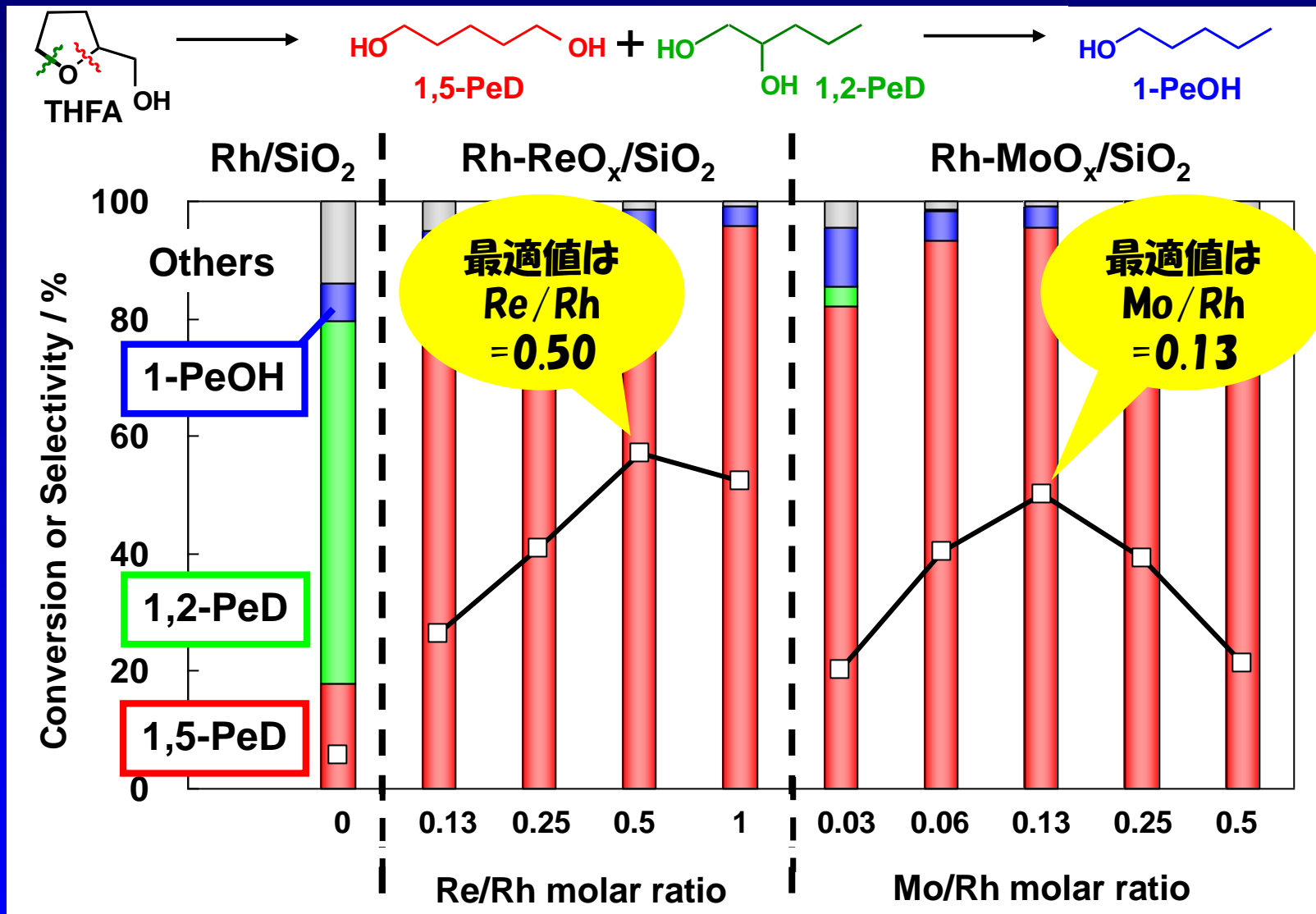


Re



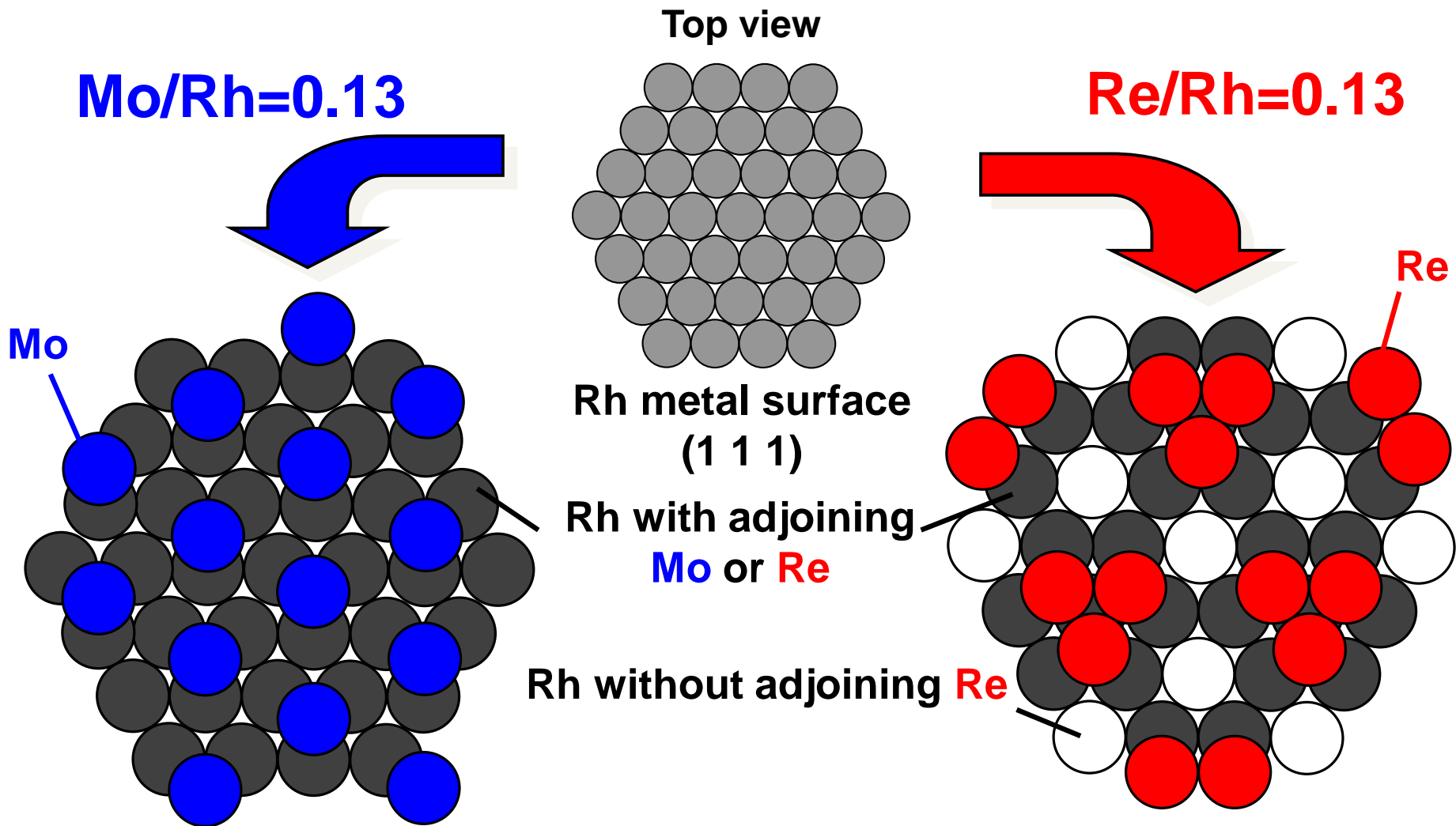
Rh表面の3-fold hollowサイト上の  
ReがReO<sub>x</sub>クラスタの形成

# Re, Mo添加量依存



Conditions :  $P = 8.0$  MPa,  $T = 393$  K,  $m_{cat} = 50$  mg,  $t = 4$  h,  
 Rh = 4 wt%, Reactant = 5 wt% THFA aqueous solution 20 ml.

Model structure of  $Rh-MO_x/SiO_2$  ( $M: Re, Mo; M/Rh=0.13$ )



すべてのRhをMoで修飾  
Mo/Rh=0.13が最適

Reで修飾されていないRhあり  
最適値はRe/Rh>0.13

# 新しい炭素—酸素結合水素化分解反应用 触媒の構造 (Ir-ReO<sub>x</sub>, Rh-ReO<sub>x</sub>, Rh-MoO<sub>x</sub>)

XRD, TEM,  
昇温水素還元, XPS,  
CO吸着量測定,  
CO吸着FTIR,  
XAFS, XANES

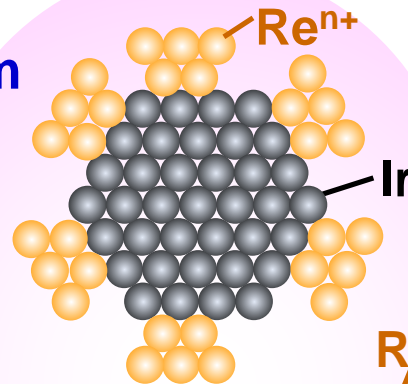
## ReO<sub>x</sub> 3-D clusters on Ir metal particles (2 nm)

(J. Phys. Chem. C, 116, 23503 (2012))

Re-O: 1.6, 0.204 nm

Re-Ir (or -Re) : 5.5, 0.265 nm

(最適比Re/Ir=1)



## ReO<sub>x</sub> 2-D clusters on Rh metal particles (3 nm)

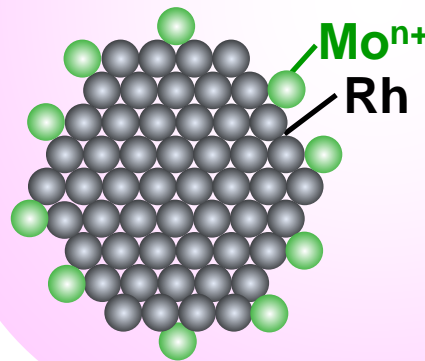
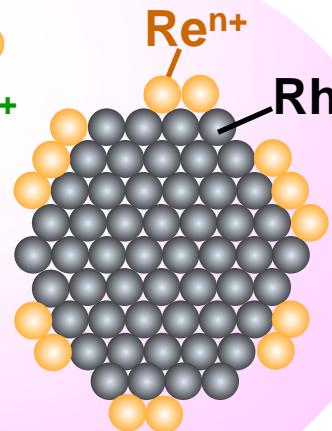
(J. Phys. Chem. C,  
116, 3079 (2012))

(最適比Re/Rh=0.5)

Re-O: 1.5, 0.209 nm

Re-Rh: 3.3, 0.265 nm

Re-Re: 2.7, 0.270 nm



## Isolated MoO<sub>x</sub> on Rh metal particles (3 nm)

(Appl. Catal. B, 111-112, 27  
(2012))

(最適比Mo/Rh=0.13)

Mo-O: 1.1, 0.208 nm

Mo-Rh (or -Mo):

3.0, 0.264 nm

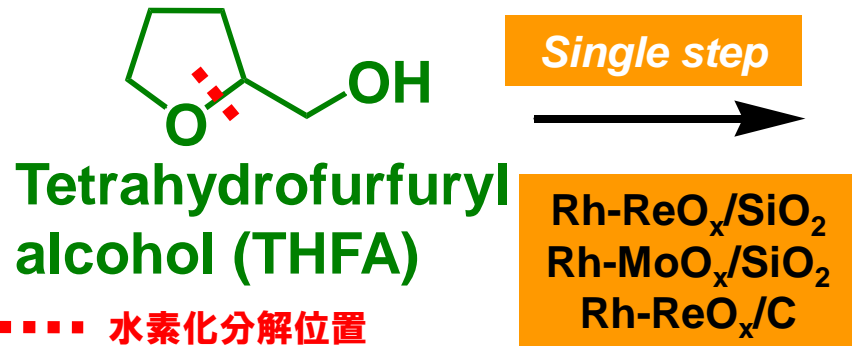
金属酸化物修飾(Re, Mo)-  
金属微粒子(Ir, Rh)触媒

吸収原子—  
散乱原子

配位数,  
結合距離

# Re及びMo酸化物修飾一金属 (IrまたはRh) 触媒 (Ir-ReO<sub>x</sub>, Rh-ReO<sub>x</sub>, Rh-MoO<sub>x</sub>) を用いた テトラヒドロフルフリアルコールの水素化分解反応による 1,5-ペンタンジオールの合成

Rh-ReO<sub>x</sub> or Rh-MoO<sub>x</sub>  
Chem. Commun. 2009  
J. Catal. 2009  
ChemCatChem 2010  
Appl. Catal. B 2012



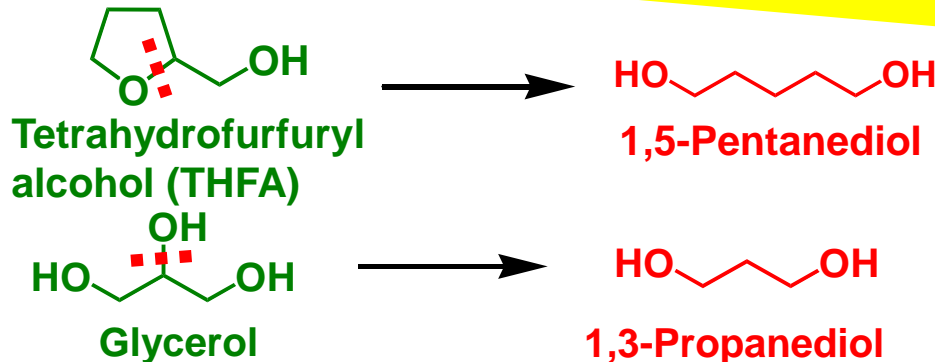
**最高収率94%**  
HO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH  
**1,5-Pentanediol**

本研究以後、他の研究者による同一触媒系の研究、THFA水素化分解研究が行われきている。

従来型触媒と比較して  
高選択性・高活性、一段階反応

..... 水素化分解位置

並行してグリセリンの  
水素化分解研究も実施

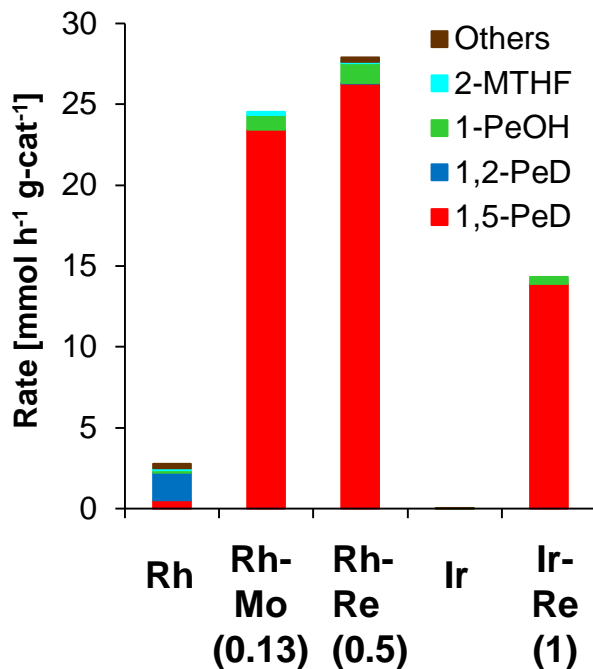
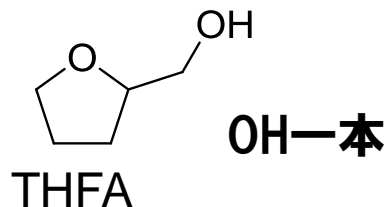


THFAとグリセリンの水素化分解の類似性:  
水素化分解位置  $\text{—O—}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{—CH}_2\text{OH}$

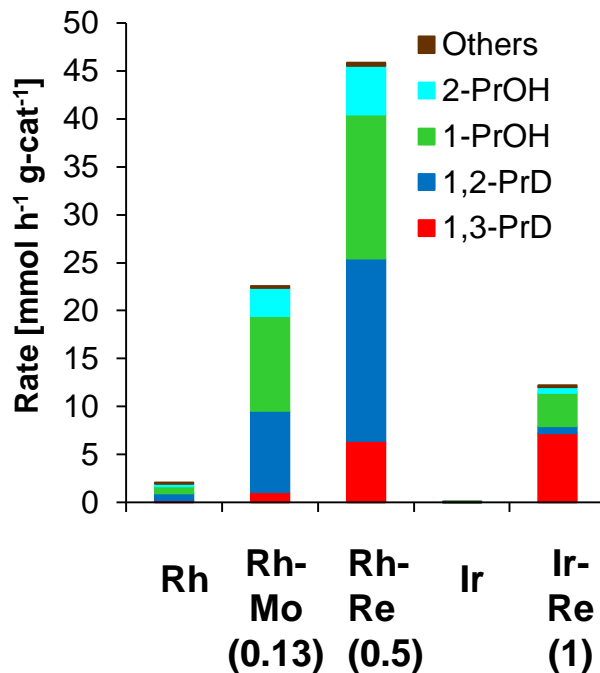
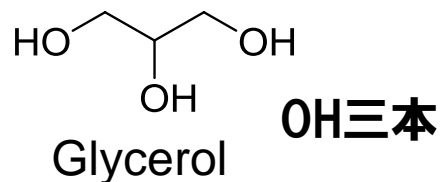
1,3-PrD選択性はRh-ReO<sub>x</sub>, Rh-MoO<sub>x</sub>では不十分  
⇒さらなる触媒探索



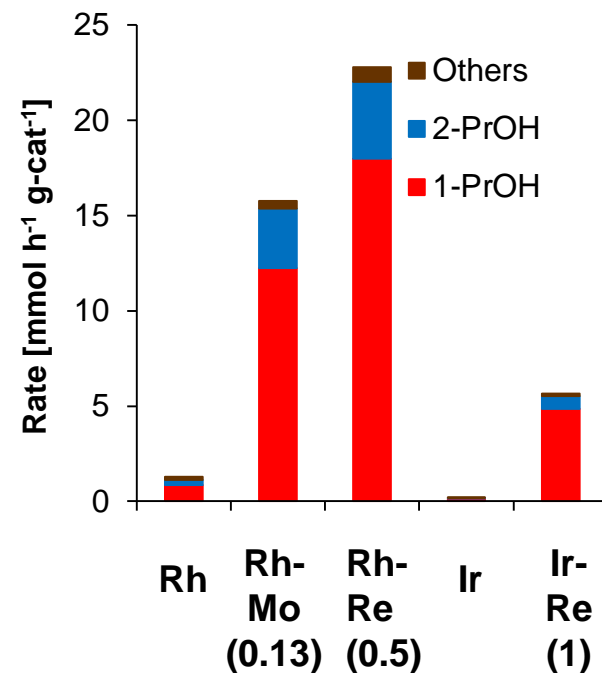
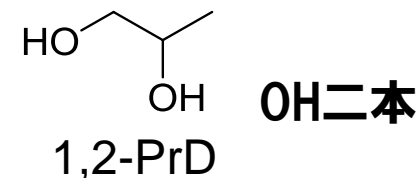
# 水素化分解の活性と選択性のまとめ



THFA, 1 g (5 wt% eq.), catal., 50 mg (for Ir-Re, 150 mg); H<sub>2</sub>, 8 MPa; H<sup>+</sup>/Re=1 (for only Ir-Re); 393 K. Time and conversion: Rh, 4 h, 5.7%; Rh-Mo, 4 h, 50.1%; Rh-Re: 4 h, 56.9%; Ir, 24 h, <0.1%; Ir-Re, 2 h, 43.9%.



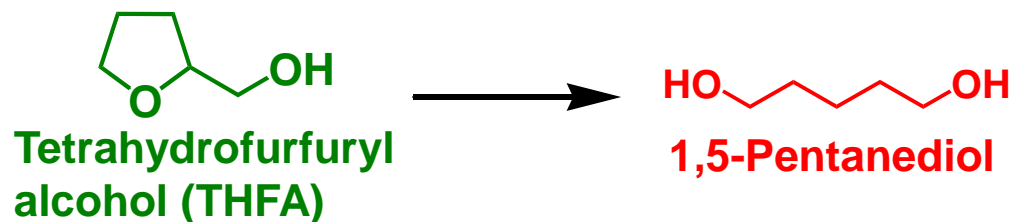
Glycerol, 4 g (67 wt% eq.; for Ir-Re, 80 wt% eq.), catal., 150 mg (for Ir, 600 mg); H<sub>2</sub>, 8 MPa; H<sup>+</sup>/Re=1 (for only Ir-Re); 393 K. Time and conversion: Rh, 5 h, 3.6%; Rh-Mo, 5 h, 38.9%; Rh-Re: 5 h, 79%; Ir, 240 h, 7.7%; Ir-Re, 12 h, 50.5%.



1,2-PrD, 4 g (20 wt% eq.), catal., 150 mg (for Ir, 300 mg); H<sub>2</sub>, 8 MPa; H<sup>+</sup>/Re=1 (for only Ir-Re); 393 K. Time and conversion: Rh, 24 h, 8.8%; Rh-Mo, 4 h, 18%; Rh-Re: 4 h, 26%; Ir, 48 h, 5.1%; Ir-Re, 24 h, 38.6%.

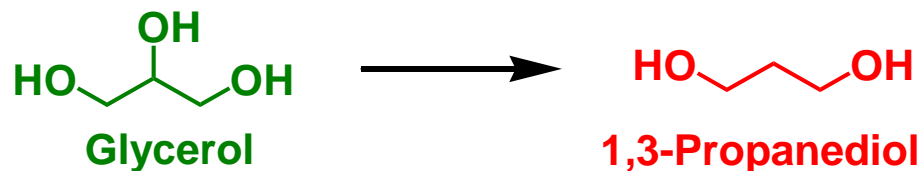
## 金属-酸化物界面を活性点とするC-O結合水素化分解反応 東北大院工 富重圭一

1. C-O結合水素化分解反応とバイオマス化学品製造
2. Rh-ReO<sub>x</sub>及びRh-MoO<sub>x</sub>触媒を用いたテトラヒドロフルフリルアルコールの水素化分解



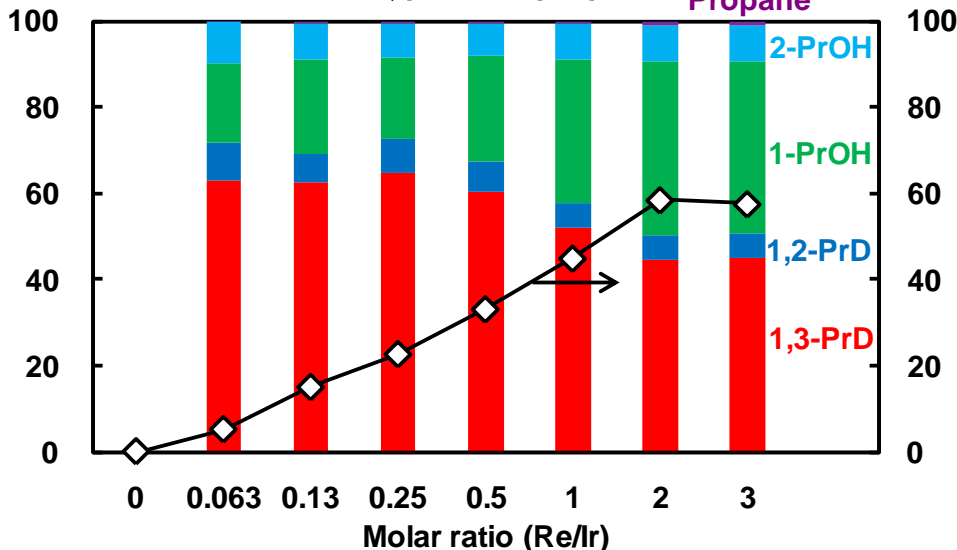
3. Ir-ReO<sub>x</sub>触媒を用いたグリセリンの水素化分解

4. Ir-ReO<sub>x</sub>構造解析



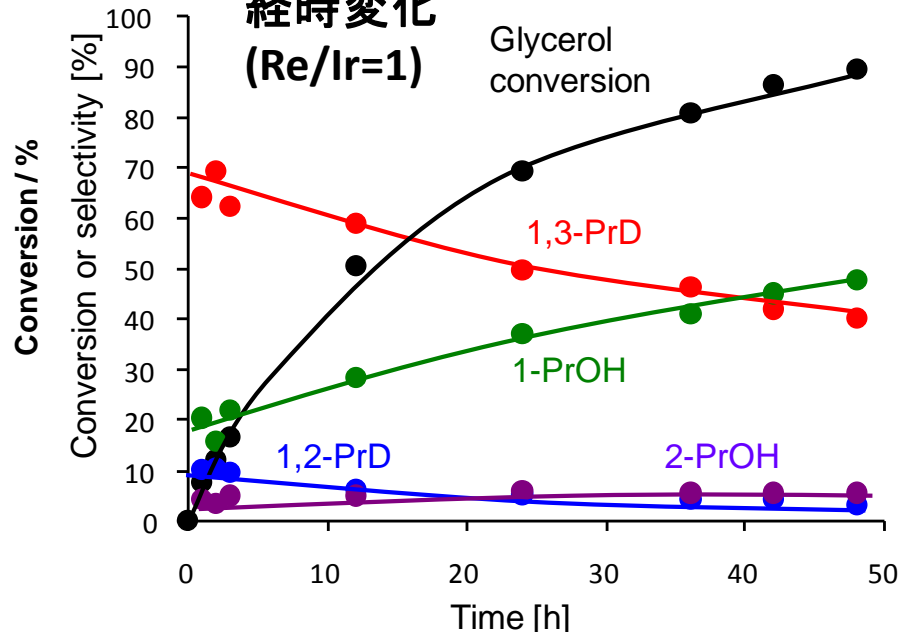
# Re酸化物修飾—Ir金属 (Ir-ReO<sub>x</sub>) 触媒上のグリセリン水素化分解

Re添加量依存



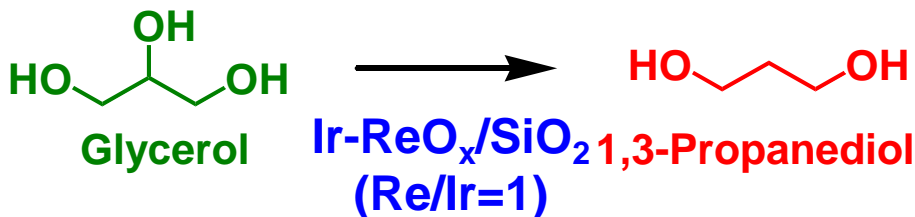
Conditions: 67 wt%Glycerol aq 6 g,  $m_{cat} = 150$  mg,  
 $T = 393$  K,  $t = 12$  h,  
 $P = 8.0$  MPa,  $H_2SO_4$  ( $H^+/Ir = 1$ ). PrD: propanediol,  
 PrOH: propanol.

経時変化  
(Re/Ir=1)



Conditions: Catalyst (150 mg), glycerol (4 g),  
 water (1 g),  $H_2$  (8 MPa),  $H_2SO_4$  ( $H^+/Ir=1$ ), 393 K.

**Ir/SiO<sub>2</sub>, ReO<sub>x</sub>/SiO<sub>2</sub>: 極めて低活性  
 IrとReの共存で触媒活性が発現**



J. Catal. 272, 191 (2010)  
 Appl. Catal. B 105, 117 (2011)

**当時の世界最高収率(38%)  
 現在も世界最高活性(58 h<sup>-1</sup> @393 K)**

他の報告例(<<10 h<sup>-1</sup> @453 K)

# グリセリンの水素化分解による1,3-PrD合成に関する報告例

| Catalyst   | Solvent      | Glycerol/M<br>(molar ratio) | Temp.<br>/ K | 1,3-PrD<br>Yield / % | TOF<br>/ h <sup>-1</sup> |
|--|--------------|-----------------------------|--------------|----------------------|--------------------------|
| <sup>a</sup> Pt/WO <sub>3</sub> /ZrO <sub>2</sub>                                  | DMI          | 290                         | 443          | 24                   | 3.9                      |
| <sup>b</sup> Pt/WO <sub>3</sub> /ZrO <sub>2</sub>                                  | None         | –                           | 403          | 32                   | –                        |
| <sup>c</sup> Cu-H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub> | None         | –                           | 443          | 27                   | –                        |
| <sup>d</sup> Pt-Re/C   | Water        | 350                         | 443          | 13                   | 4.0                      |
| <sup>e</sup> Pt/WO <sub>3</sub> /TiO <sub>2</sub> /SiO <sub>2</sub>                | Water        | 210                         | 453          | 8                    | 1.5                      |
| <sup>f</sup> Pt/sulfated ZrO <sub>2</sub>  | DMI          | 280                         | 443          | 56                   | 0.7                      |
| <sup>g</sup> Pt/WO <sub>x</sub> /AlOOH   | Water        | 110                         | 453          | 66-69                | 6.1                      |
| <sup>h</sup> Rh-ReO <sub>x</sub> /SiO <sub>2</sub>                                 | Water (none) | 750                         | 393          | 11                   | 1.7                      |
| <sup>i</sup> Ir-ReO <sub>x</sub> /SiO <sub>2</sub>                                 | Water (none) | 1390                        | 393          | 38                   | 15 (36 h)                |
| <sup>i</sup> Ir-ReO <sub>x</sub> /SiO <sub>2</sub>                                 | Water (none) | 1390                        | 393          | 8                    | 58 (2 h)                 |

**Pt/WO<sub>x</sub>/AlOOH:1,3-PrD高収率 金田(大阪大)**

**Ir-ReO<sub>x</sub>/SiO<sub>2</sub>: 2010年当時最高収率、現時点でも最高TOF(触媒回転速度)、他例より低温。**

J. Catal. 272, 191 (2010)  
Appl. Catal. B 105, 117 (2011)

<sup>a</sup>Y. Sasaki, et al., *Catal. Commun.*, 9 (2008) 1360.

<sup>b</sup>C.L. Chen et al., *Green Chem.* 12 (2010) 1466.

<sup>c</sup>L.Huang et al., *Catal. Lett.* 131 (2009) 312.

<sup>d</sup>R.J. Davis et al., *ChemCatChem* 7 (2010) 1107.

<sup>e</sup>Y. Ding et al., *Appl. Catal. A* 390 (2010) 119.

<sup>f</sup>H.Lee et al., *Green Chem.* 13 (2011) 2004.

<sup>g</sup>K. Kaneda et al., *ChemSusChem* 6 (2013) 1345.

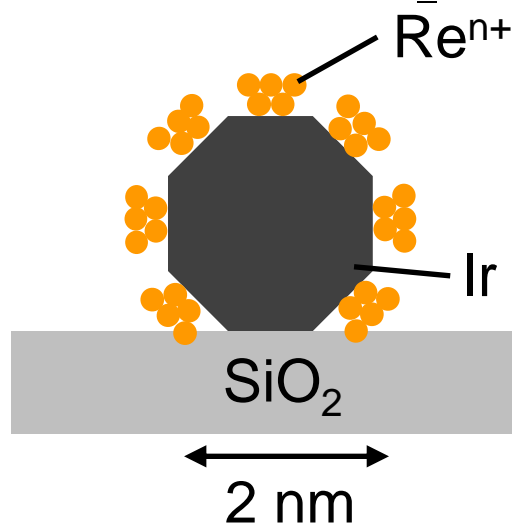
<sup>h</sup>Y. Shinmi et al., *Appl. Catal. B* 94 (2010) 318.

<sup>i</sup>Y. Nakagawa et al., *J. Catal.* 105 (2010) 191.

## 触媒解析手法

|               |  |
|---------------|--|
| XRD           | ・ ・ ・ Ir 粒子径, 金属(Ir)の酸化状態                |
| TEM           | ・ ・ ・ Ir 粒子径                             |
| TPR, XPS      | ・ ・ ・ 金属(Ir, Re)の酸化状態                    |
| CO-adsorption | ・ ・ ・ 表面Irメタル量                           |
| XAFS, XANES   | ・ ・ ・ 金属(Ir, Re)の酸化状態, 配位状態, 粒子径(Ir, Re) |

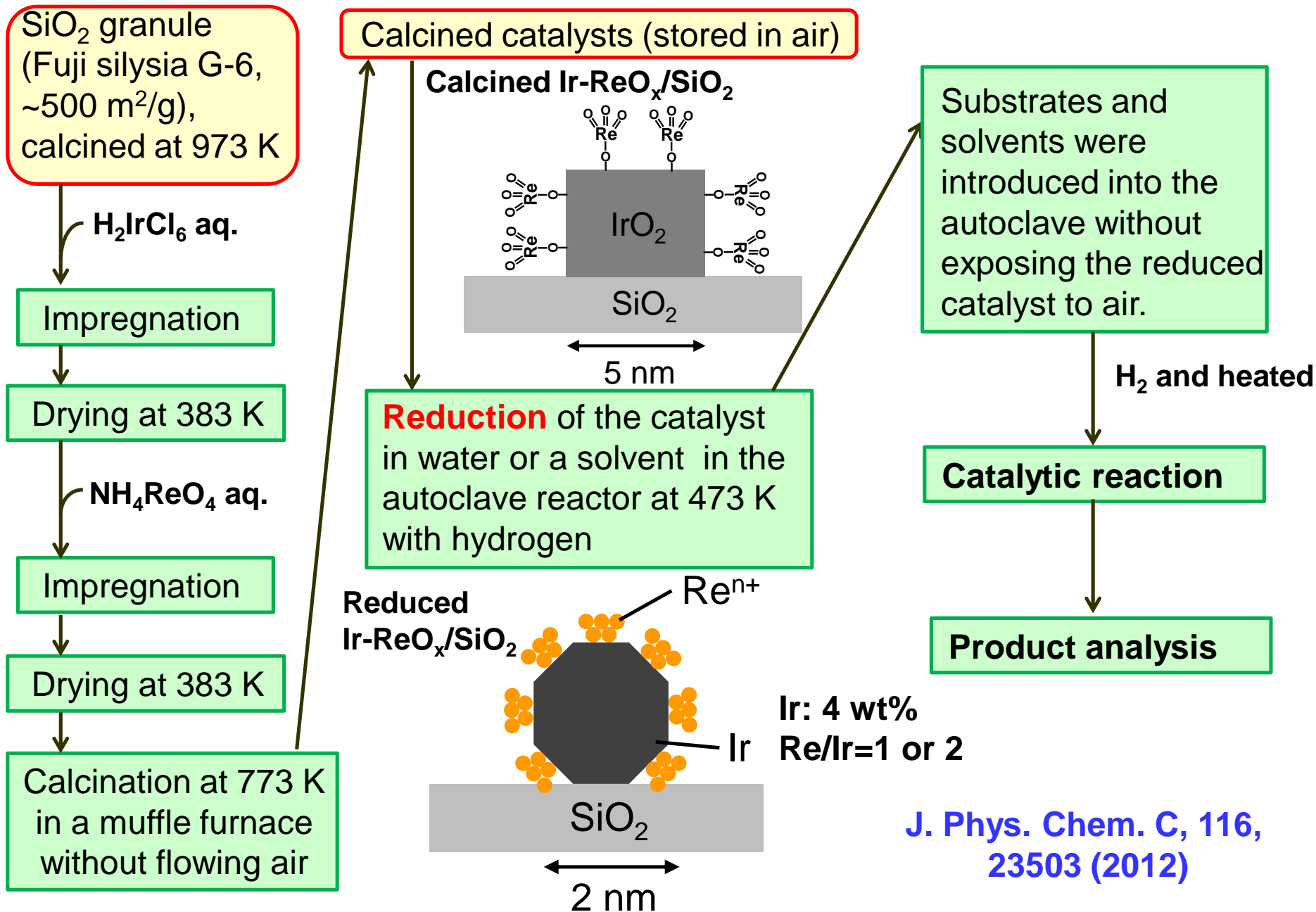
## Image of Ir-ReO<sub>x</sub>/SiO<sub>2</sub>



- Irはメタル状態
- Irの粒子径は2 nm程度
- Reは低原子価(+2~+3)の酸化物
- Ir上にReO<sub>x</sub>が集積した

三次元クラスター構造

# Ir-ReO<sub>x</sub>/SiO<sub>2</sub>触媒の調製

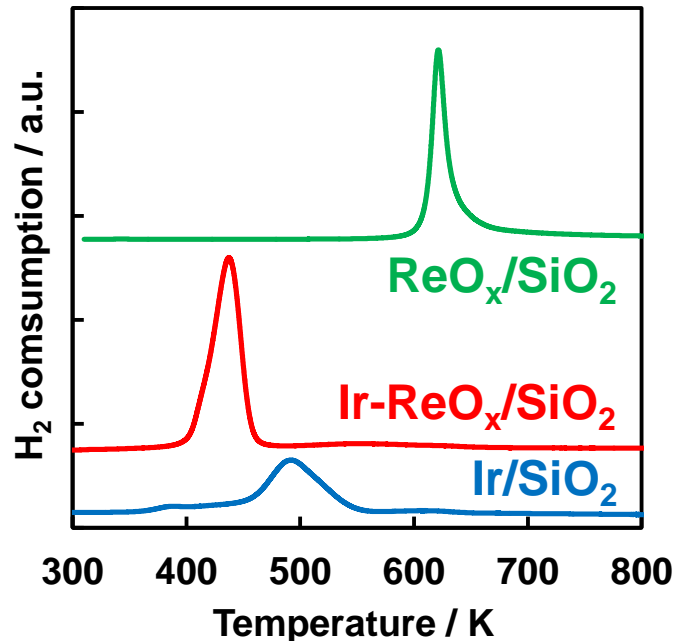


# 実験: 触媒調製

- **Ir-ReO<sub>x</sub>/SiO<sub>2</sub>** ... Ir: 4 wt%, **Re/Ir = 1** (モル比)
- 担体: SiO<sub>2</sub> (富士シリシア G-6 (比表面積: 535 m<sup>2</sup> · g<sup>-1</sup>)), 973 K, 1 h 焼成
- 金属前駆体: H<sub>2</sub>IrCl<sub>6</sub> aq, NH<sub>4</sub>ReO<sub>4</sub>      触媒調製法: 逐次含浸法

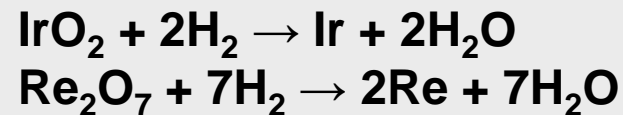
## 水素昇温還元測定(H<sub>2</sub>-TPR)

Y. Nakagawa et al., *J. Catal.*, 2010, 272, 191.  
Y. Amada et al., *Appl. Catal. B*, 2011, 105, 117.



5% H<sub>2</sub>/Ar, 5 K/min (Ir and Ir-ReO<sub>x</sub>) or  
10 K/min (ReO<sub>x</sub>) heating rate, 0.01 g-cat.

| 水素消費量 / mol          | Ir価数 | Re価数 |
|----------------------|------|------|
| $2.8 \times 10^{-5}$ | —    | 1.6  |
| $4.4 \times 10^{-5}$ | 0    | 2.5  |
| $2.0 \times 10^{-5}$ | 0    | —    |



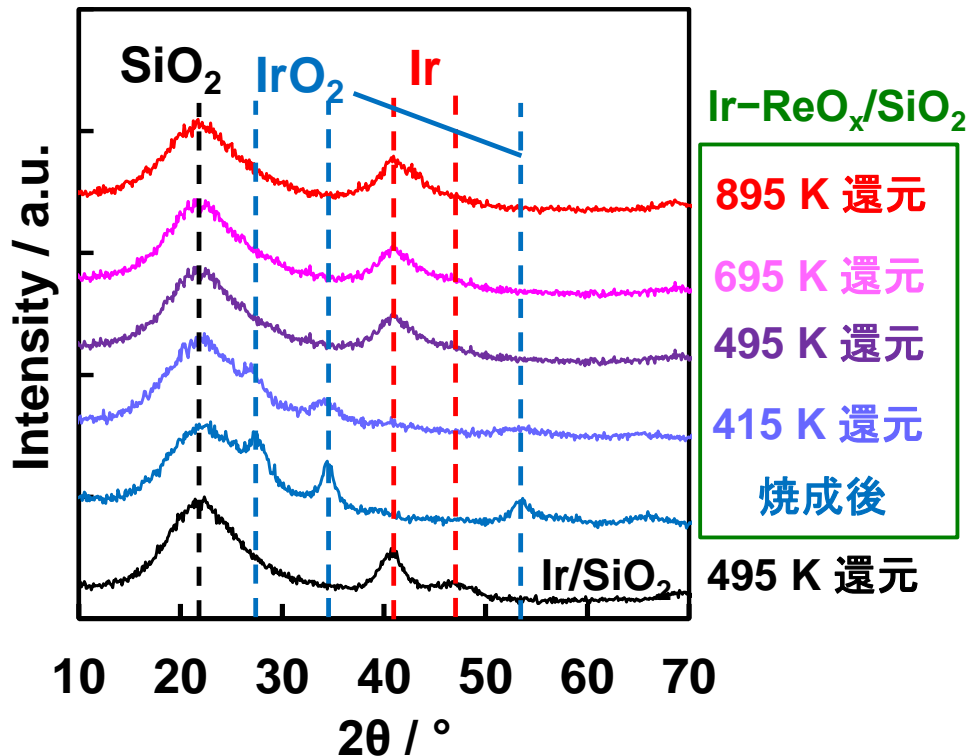
• Ir-ReO<sub>x</sub>/SiO<sub>2</sub>はIr/SiO<sub>2</sub>及びReO<sub>x</sub>/SiO<sub>2</sub>の単独触媒に比べ低温で還元が進行

➡ Ir種とRe種の相互作用

# XRD, CO吸着; Ir/SiO<sub>2</sub>, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

| 触媒  | 還元温度<br>/ K | Ir粒子径<br>/ nm<br>XRD | 分散度 ( $D_{XRD}$ )<br>/ %<br>XRD | 分散度 ( $D_{CO}$ )<br>/ %<br>CO吸着 <sup>a</sup> | ( $D_{XRD} - D_{CO}$ ) <sup>b</sup><br>/ % |
|---|-------------|----------------------|---------------------------------|--|--|
| Ir/SiO <sub>2</sub>                                     | 495         | 3.6                  | 31                              | 23   | 8  |
| Ir-ReO <sub>x</sub><br>/SiO <sub>2</sub><br>(Re/Ir = 1) | 415         | -                    | -                               | 7  | -  |
|   | 495         | 2.0                  | 53                              | 16   | 37   |
|   | 695         | 1.9                  | 56                              | 14   | 42   |
|   | 895         | 2.0                  | 53                              | 11   | 42   |

ReがIr金属の凝集を抑制



<sup>a</sup>FT-IRより, Ir上のCOは非解離吸着 (2068 cm<sup>-1</sup>)  
<sup>b</sup>XRDとCO吸着から見積もられる分散度の差

**Ir-ReO<sub>x</sub>/SiO<sub>2</sub>**

- ・XRD (495-895 K還元)  
Irは約2 nmのメタルとして存在
- ・CO吸着 (495-895 K還元)  
 $D_{CO}$  (11-16%) <<  $D_{XRD}$  (53-56%)

➔  $D_{XRD} - D_{CO}$ は約40%より, 表面に露出しているIr金属の大部分はReO<sub>x</sub>で被覆



# 実験方法

## TPR-XAFS

(Temperature Programmed Reduction-X-ray Absorption Fine Structure)

→水素流通下で昇温させることで、触媒を還元させながら連続的にXAFS測定を行う手法

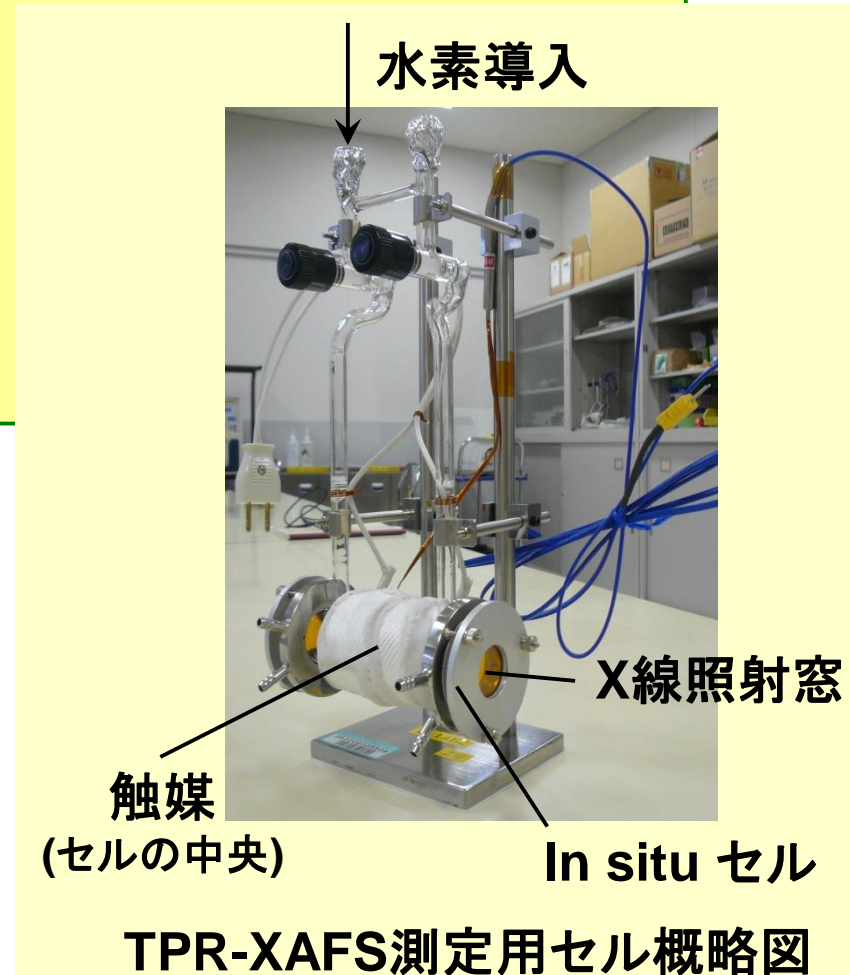
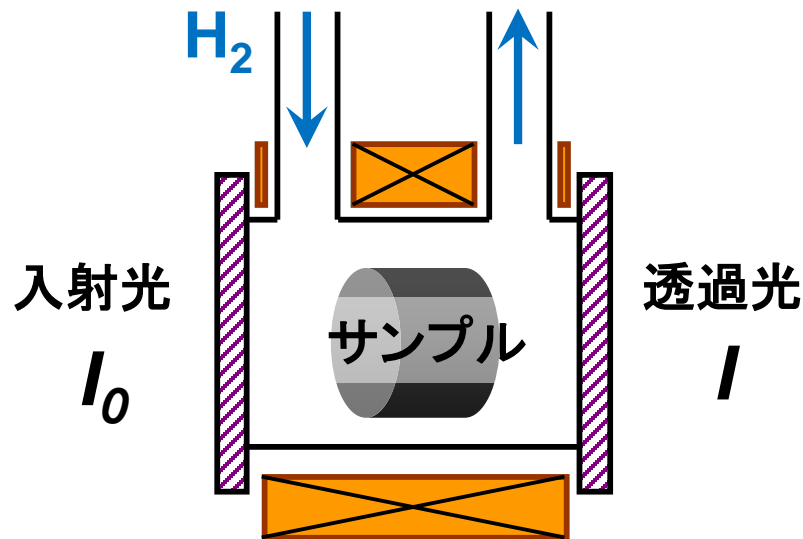
### 実験方法

流通ガス: 5%水素/アルゴン

ガス流量: 30 ml/min

昇温速度: 5 K/min

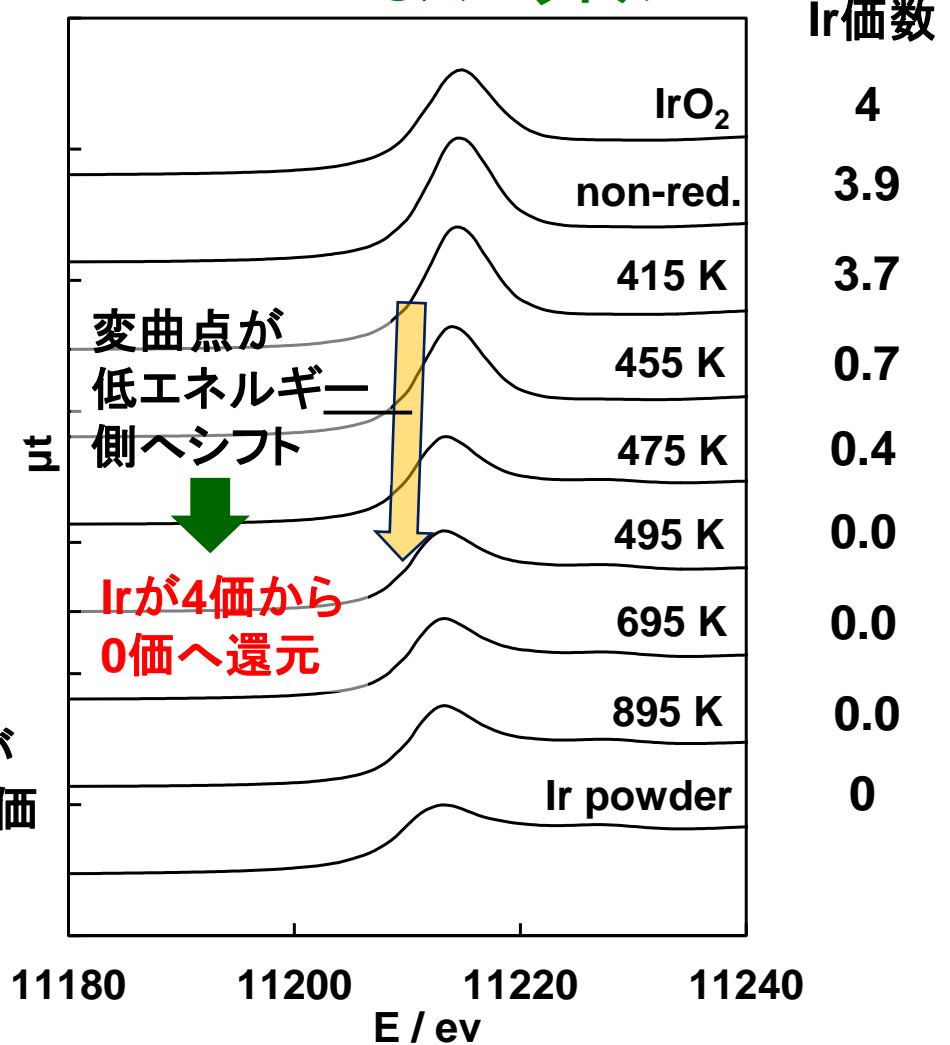
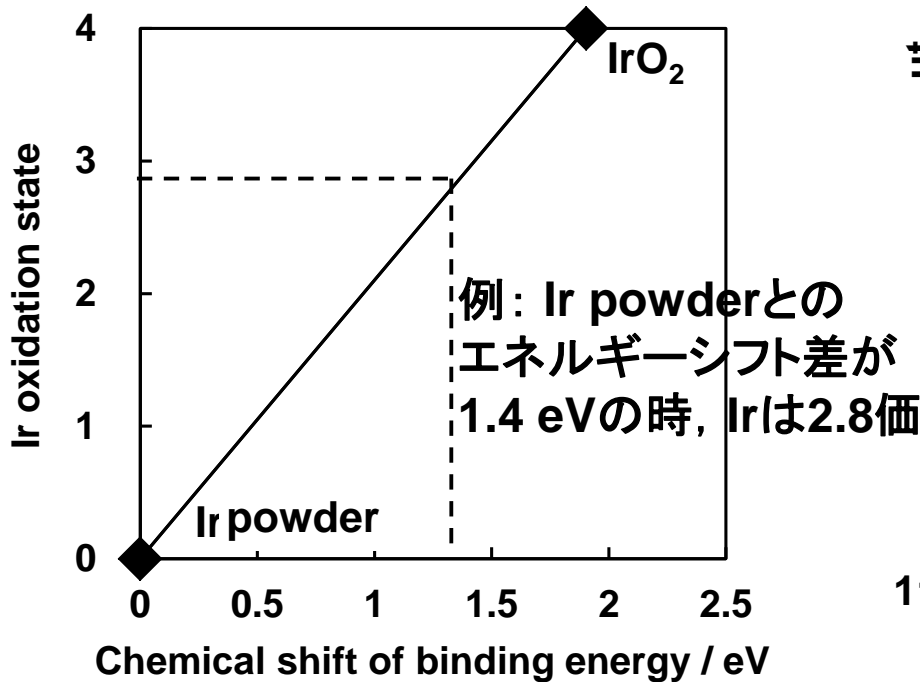
測定時間: 1 min (2分ごとに1回測定)



# Ir $L_3$ -edge XANES; Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

## XANESスペクトル

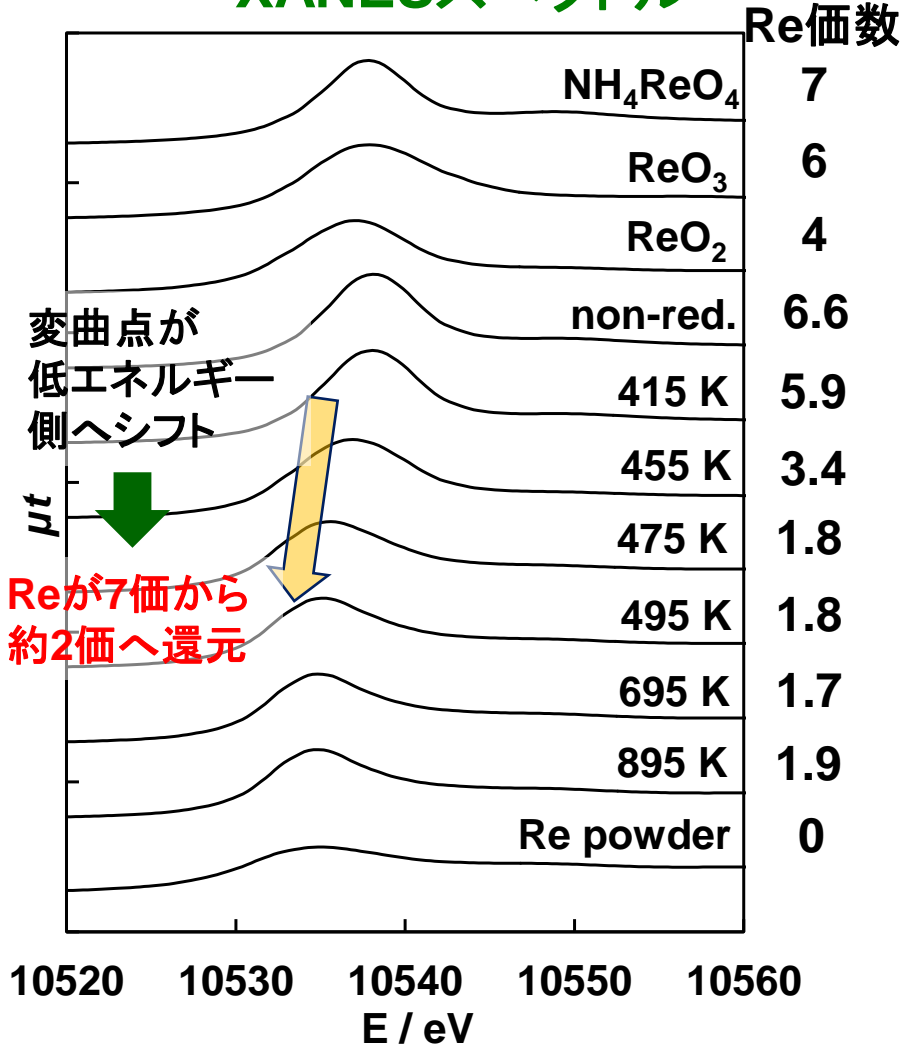
**XANESで価数を見積もる手法**  
**Pre-edgeの変曲点のエネルギーシフト差を利用**



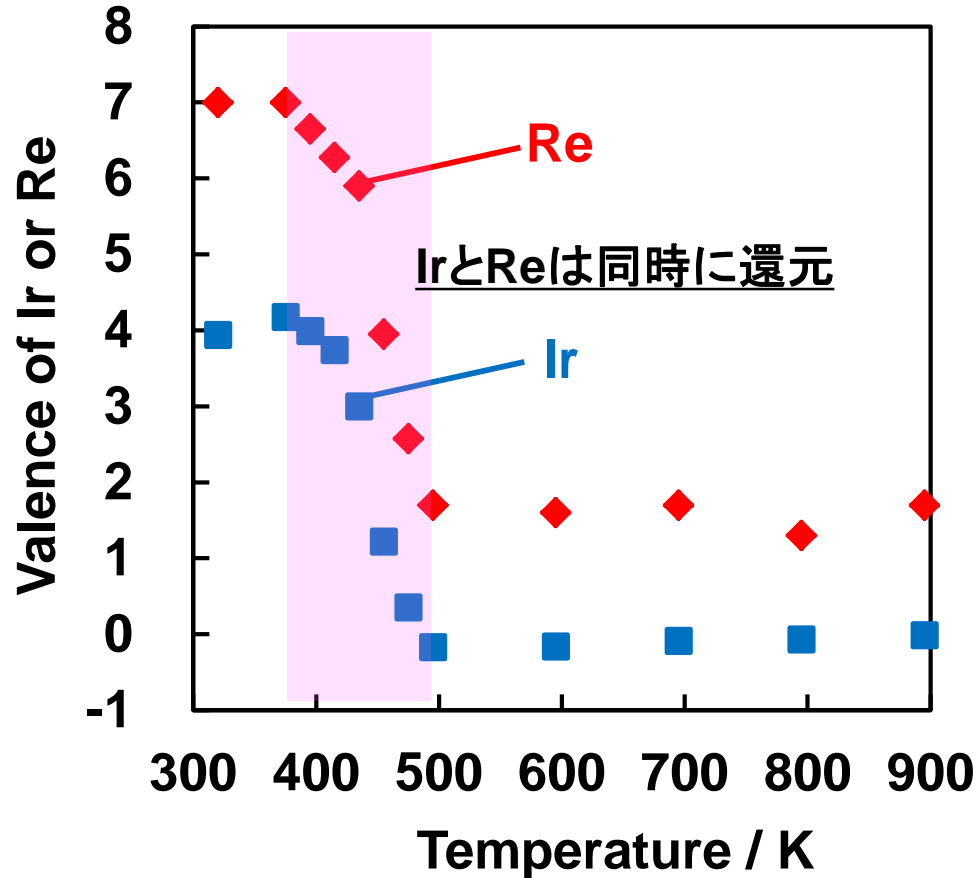
**Irは415-495 KでIr<sup>+4</sup>からIr<sup>0</sup>へ還元**

# Re $L_3$ -edge XANES; Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

## XANESスペクトル



## XANES結果まとめ



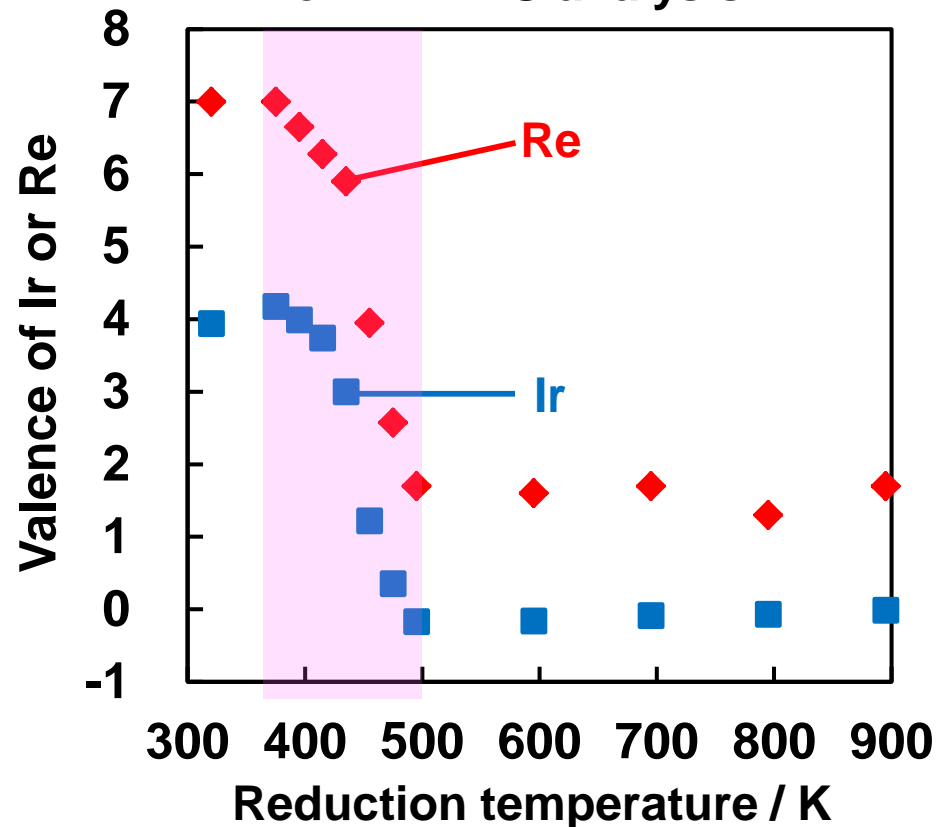
**IrとReは同時に還元 (385-495 K)**  
 495 KでIr種はメタル (XRDと一致),  
 Re種は2価程度で存在  
 (TPR, XPSと一致)

Reも415-495 Kで還元が進行 (Re<sup>7+</sup>→Re<sup>2+</sup>)

# Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1); XANES and XPS

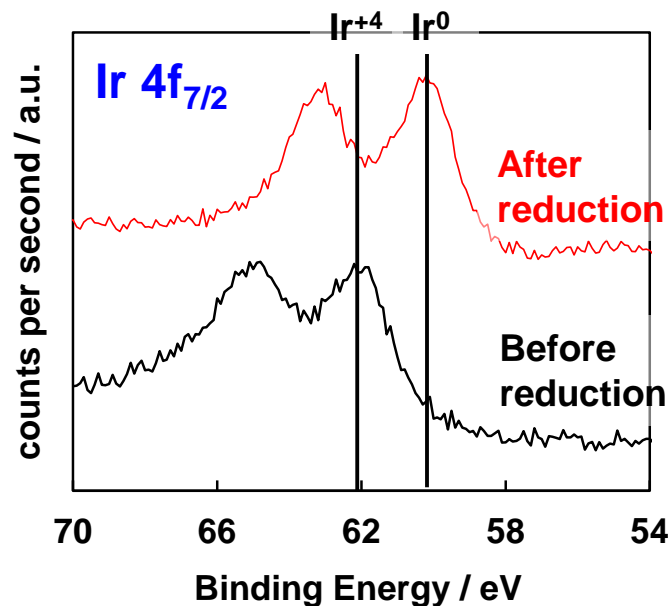
J. Phys. Chem. C, 116, 23503 (2012)

Valence of Ir or Re  
from XANES analysis



Ir and Re species are simultaneously reduced (415~495 K).

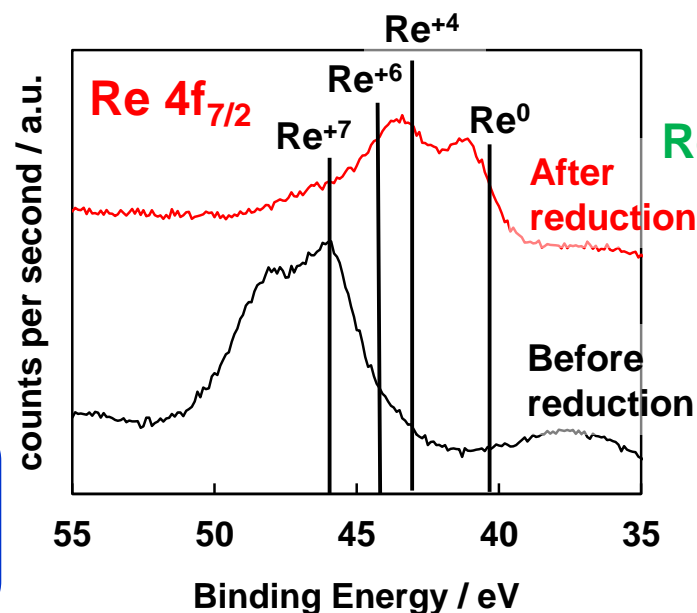
XANES and XPS indicate that Ir and Re species exists in metal Ir and low-valence Re after the reduction at 495 K.



Ir<sup>0</sup>

↑

Ir<sup>4+</sup>

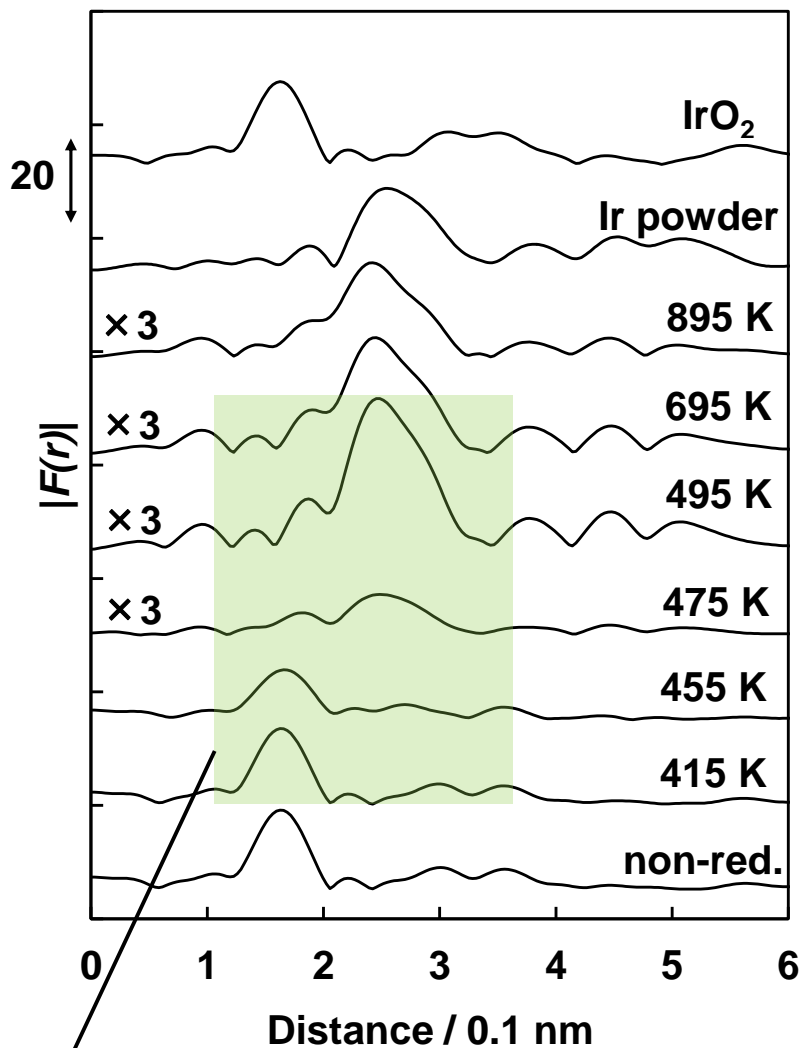


Re<sup>δ+</sup> (0 < δ < 4+)

↑

Re<sup>7+</sup>

## フーリエ変換後のスペクトル



415-495 Kの領域でIrの還元は進行

## カーブフィッティング結果

| 還元温度 / K<br>(標準サンプル) | 配位数  |                   |
|----------------------|------|-------------------|
|                      | Ir-O | Ir-Ir<br>(or -Re) |
| non-red.             | 6.0  | -                 |
| 415                  | 6.0  | -                 |
| 455                  | 4.3  | 2.3               |
| 475                  | 0.7  | 8.9               |
| 495                  | -    | 10.8              |
| 695                  | -    | 10.8              |
| 895                  | -    | 10.8              |
| Ir powder            | -    | 12                |
| IrO <sub>2</sub>     | 6    | -                 |

Fourier filtering range: 0.126-0.322 nm.

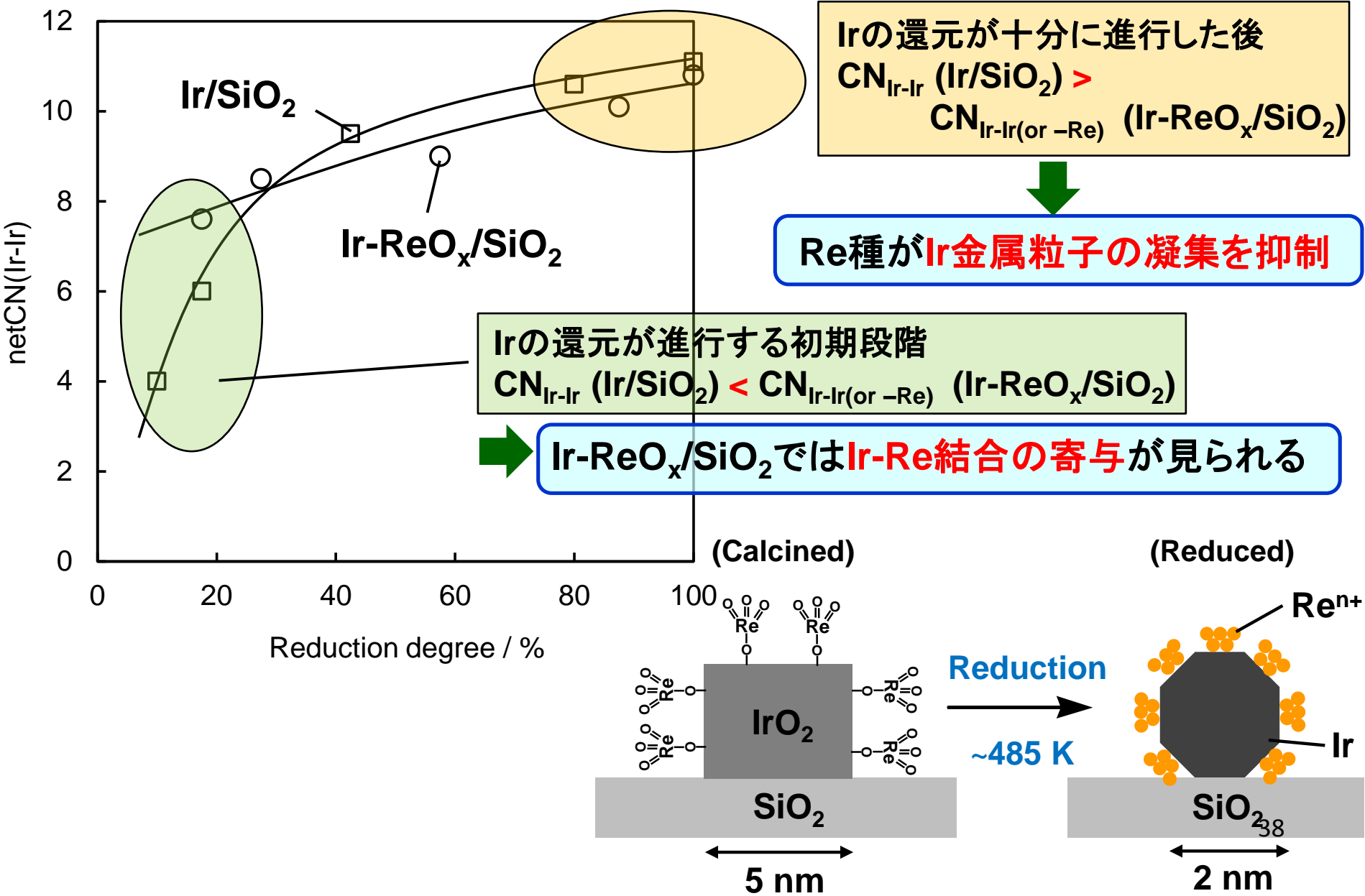
Ir種が徐々に還元され、  
Ir金属粒子が成長する

Ir金属の凝集は  
見られない  
(XRDと一致)

結合距離 Ir-O: 0.198 nm ( $\pm 0.002$ )

Ir-Ir ( or -Re): 0.276 nm ( $\pm 0.001$ )

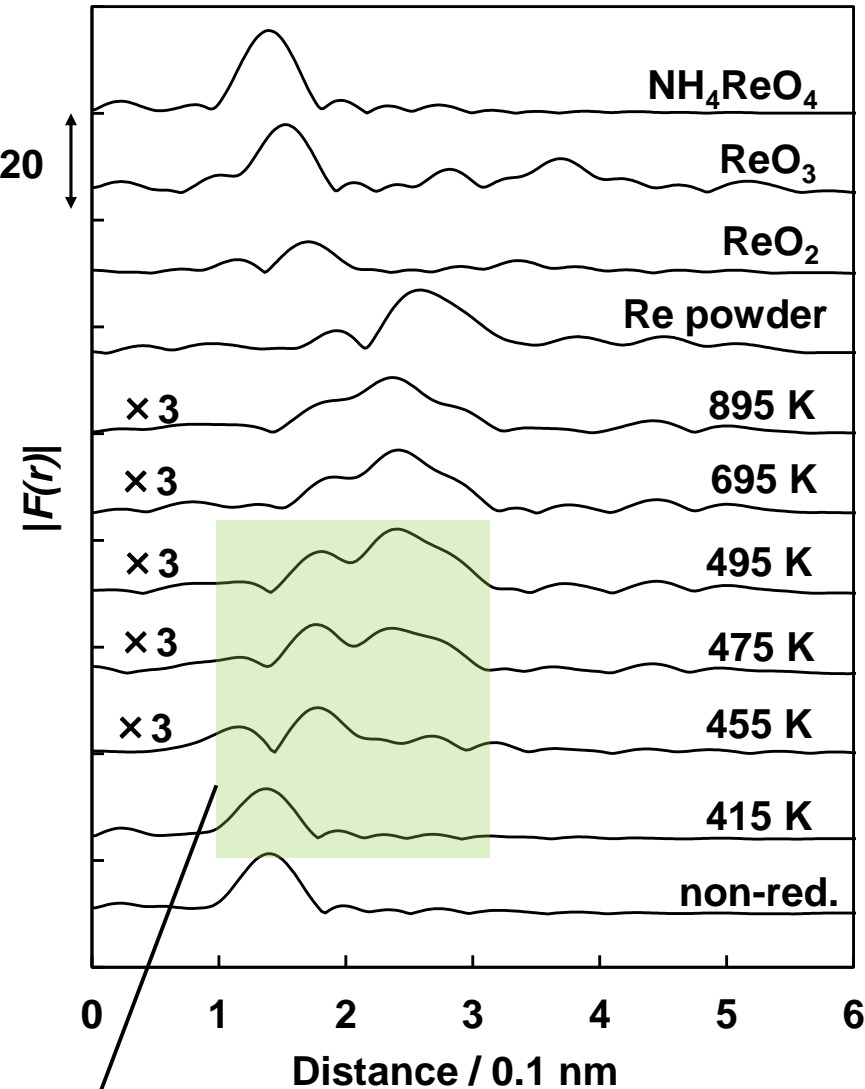
# Ir/SiO<sub>2</sub>及びIr-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)のIr金属粒子成長過程におけるIr-Ir(or -Re)配位数の比較



# Re $L_3$ -edge EXAFS; Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

## フーリエ変換後のスペクトル

## カーブフィッティング結果



| 還元温度 / K<br>(標準サンプル)             | 配位数  |            |                   |
|----------------------------------|------|------------|-------------------|
|                                  | Re=O | Re-O       | Re-Ir<br>(or -Re) |
| non-red.                         | 4.0  | -          | -                 |
| 415                              | 3.3  | 0.5        | -                 |
| 455                              | 1.0  | 2.5        | 1.4               |
| 475                              | 0.4  | 2.0        | 4.6               |
| <b>495</b>                       | -    | <b>1.6</b> | <b>6.5</b>        |
| <b>595</b>                       | -    | <b>1.6</b> | <b>6.5</b>        |
| 695                              | -    | 1.7        | 6.9               |
| 895                              | -    | 1.7        | 7.7               |
| Ir powder                        | -    | -          | 12                |
| NH <sub>4</sub> ReO <sub>4</sub> | 4    | -          | -                 |

Fourier filtering range: 0.092-0.316 nm. 徐々に増加  
**Re-Ir (or -Re)の配位数は約6.5で一度安定**

結合距離(R) Re=O: 0.174 nm (±0.002)  
 Re-O: 0.205 nm (±0.002)  
 Re-Ir ( or -Re): 0.272 nm (±0.001)

Irと同様の415-495 KでReの還元が進行

$R(\text{Ir-Ir}) > R(\text{Re-Ir}) \leftarrow \text{Reはややカチオニック}$

# 触媒構造モデル①; Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

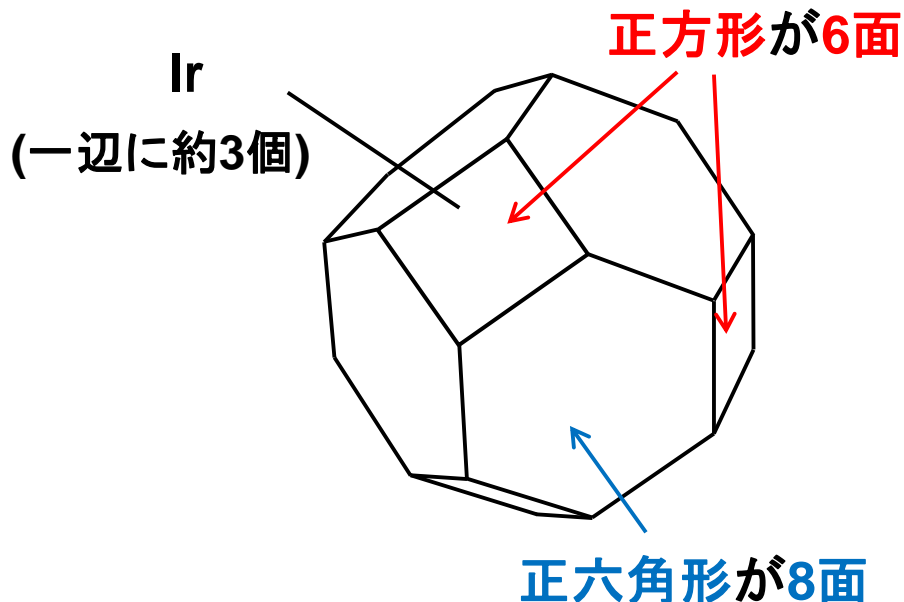
495 K還元後のIr-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)のXRD及びCO吸着結果

| Ir金属粒子径 / nm |     | 分散度 ( $D_{\text{XRD}}$ ) / % | 分散度 ( $D_{\text{CO}}$ ) / % | ( $D_{\text{XRD}} - D_{\text{CO}}$ ) / % |
|--------------|-----|------------------------------|-----------------------------|--|
| XRD          | TEM | XRD                          | CO吸着                        |  |
| 2.0          | 2.0 | 53                           | 16                          | 37                                       |

・Ir L<sub>3</sub>-edge EXAFS測定 of Ir-Ir (or -Re)配位数10.8 (495 K還元後)から算出される金属分散度(約40~50%)はXRDと一致する

## Irの構造モデル(495 K還元後の安定な状態)

➡ Cuboctahedron構造を仮定



・Ir金属粒子径 (2 nm)と  
Ir金属結合半径 (0.138 nm)より  
一辺に含まれるIrの個数は約3個  
この時,  
モデルの全原子数は201個,  
表面原子数は122個  
分散度は61%(= 122/201)



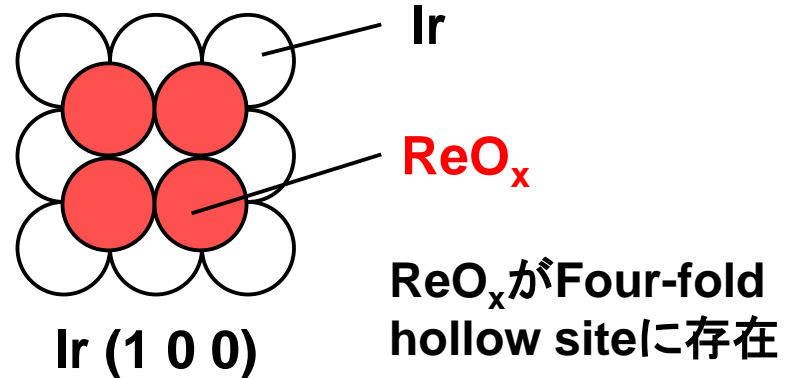
# 触媒構造モデル②; Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

## ReO<sub>x</sub>の構造モデルを検討

Irを被覆する第一層の  
ReO<sub>x</sub>の割合は,  
D<sub>XRD</sub>-D<sub>CO</sub>より37%

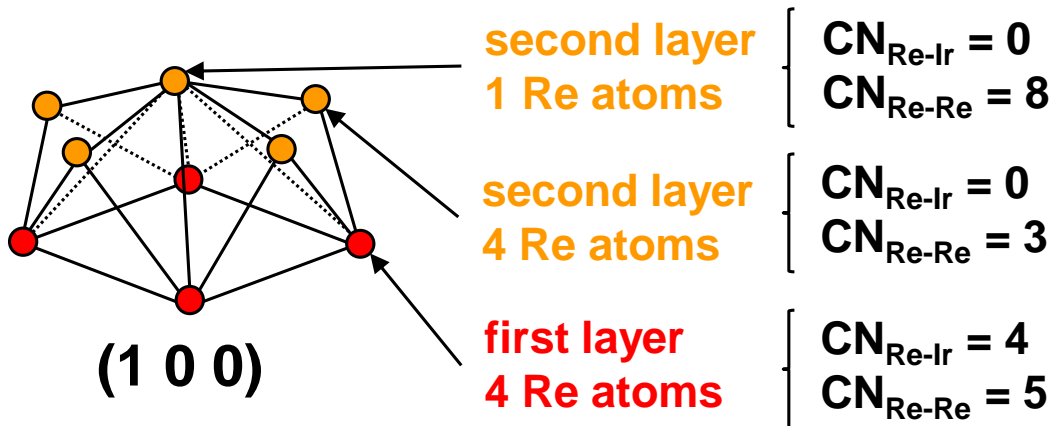
残りのReO<sub>x</sub>(63%)が  
第二層に存在すると仮定

## 表面のIr原子と第一層のReO<sub>x</sub>



このモデルにおいて, Ir表面を被覆する  
第一層のReO<sub>x</sub>の割合は44% (=4/9)

## 第一層のReO<sub>x</sub>と第二層のReO<sub>x</sub>

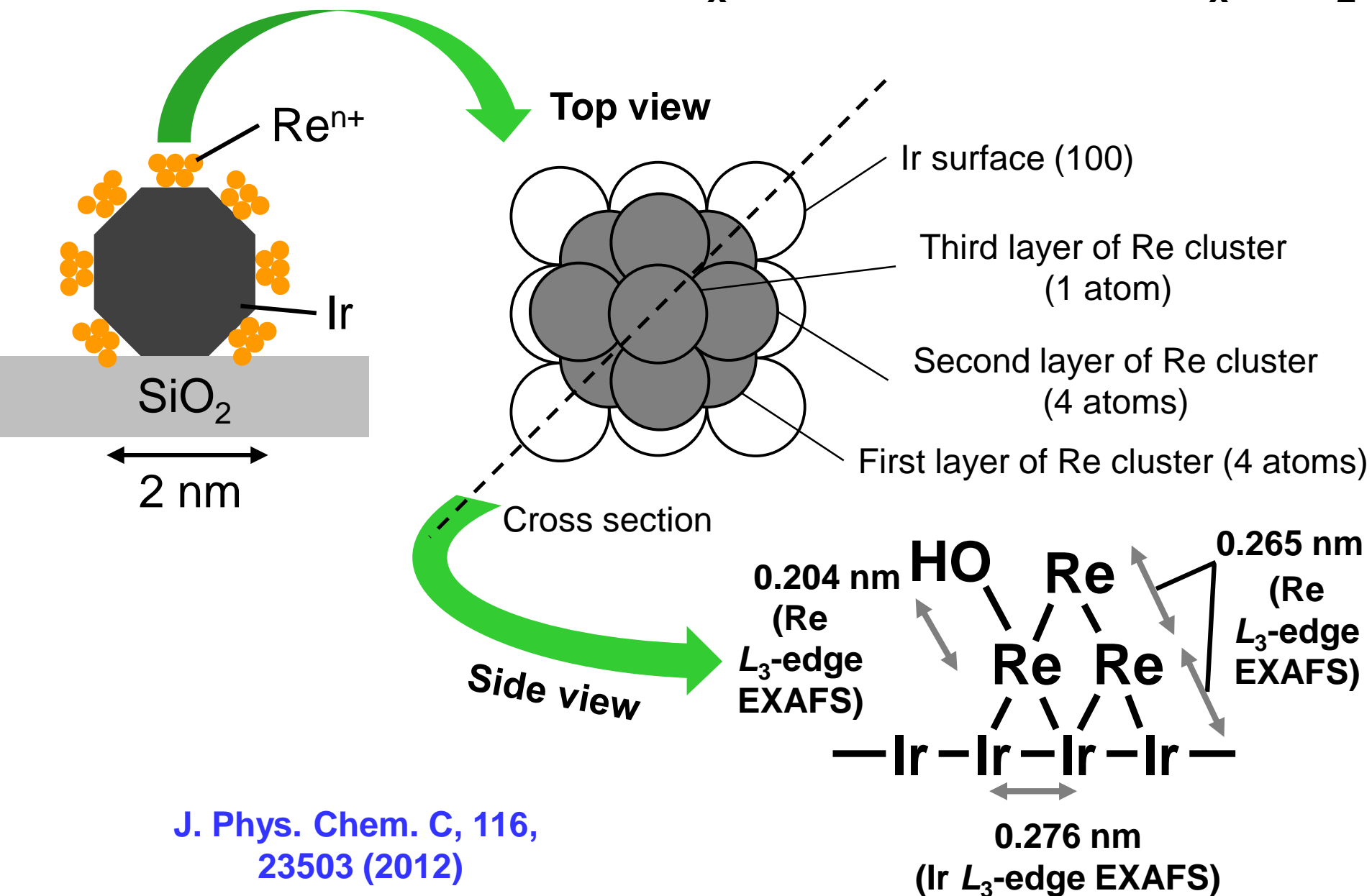


CN<sub>Re-Ir (or -Re)</sub>の平均値;  
(1 × 8 + 4 × 3 + 4 × 9)/9 = 6.2

EXAFSで得られた  
CN<sub>Re-Ir (or -Re)</sub> = 6.5と一致

このモデルの第二層のReO<sub>x</sub>の割合は56% (=5/9)

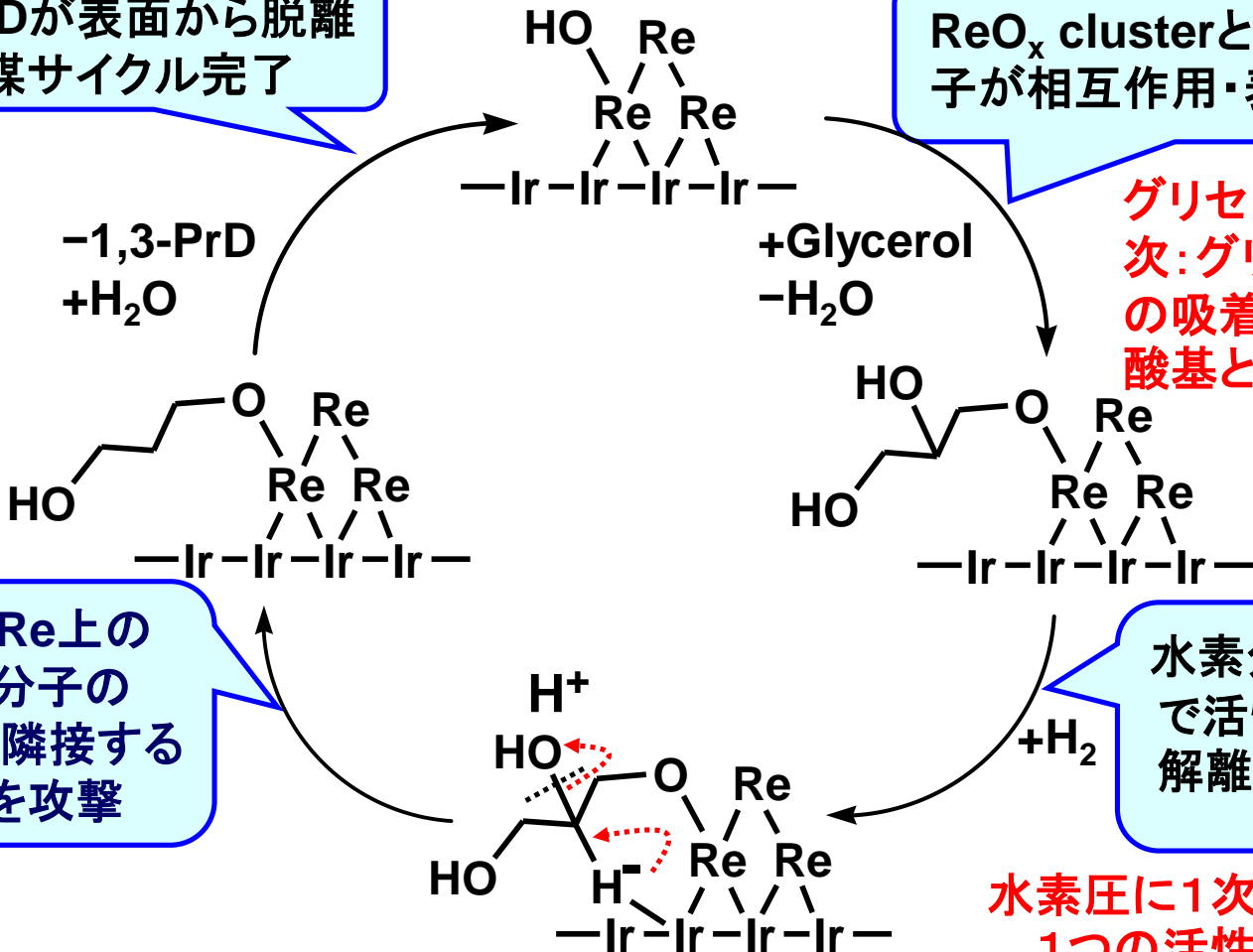
# Model structure of 3D-ReO<sub>x</sub> clusters on Ir-ReO<sub>x</sub>/SiO<sub>2</sub>



# Ir金属微粒子-ReO<sub>x</sub>クラスター界面が触媒活性点となる ハイドライド攻撃による直接水素化分解機構

1,3-PrDが表面から脱離し、触媒サイクル完了

ReO<sub>x</sub> clusterとグリセリン分子が相互作用・表面に固定



グリセリン濃度にゼロ次:グリセリンの触媒への吸着は強い(1級水酸基との相互作用強)。

Ir上のH<sup>-</sup>がRe上のグリセリン分子の-CH<sub>2</sub>OH基に隣接する炭素原子を攻撃

水素分子がIr金属上で活性化し、不均等解離によりH<sup>-</sup>とH<sup>+</sup>が生成

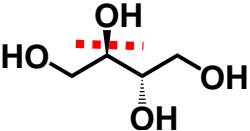
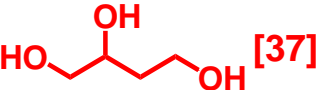
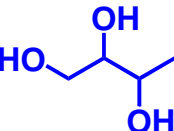
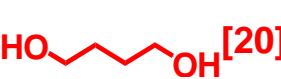
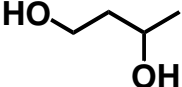
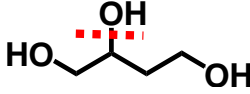

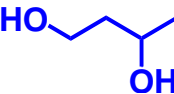
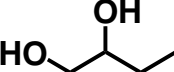
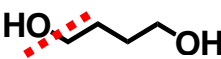
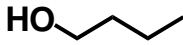
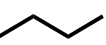
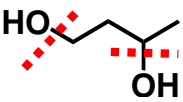
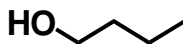
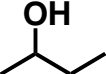
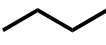
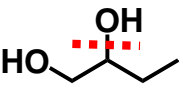
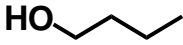
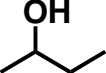
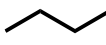
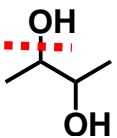
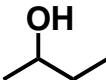
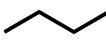

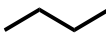
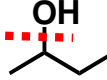
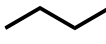
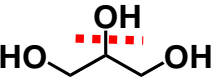
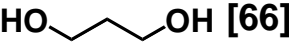
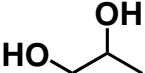


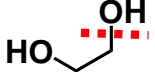
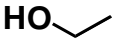
水素圧に1次:水素1分子から1つの活性水素種の生成 (kinetics, THFA+D<sub>2</sub>反応)

上のReは下のRe-O結合の動きを制限し、ハイドライド攻撃の選択性を向上 (グリセリンの場合に顕著)

THFAでも類似した反応機構

J. Catal. 272, 191 (2010)  
 Appl. Catal. B 105, 117 (2011)  
 J. Catal., 243, 171 (2012)

# Ir-ReO<sub>x</sub>/SiO<sub>2</sub>上のポリオールの水素化分解 ChemSusChem 5, 1991 (2012)

| Entry | Substrate   | Conv. / % | Products [selectivity / %]  |  |  |   |             |
|-------|---|-----------|---|--|--|---|-------------|
| 1     |    | <b>26</b> |  [37]    |  [21]  |  [20]   |  [8]   | Others [14] |
| 2     |    | <b>51</b> |  [73]    |  [12]  |  [7]    | Others [7]  |             |
| 3     |    | <b>12</b> |  [97]    |  [3]   |  |   |             |
| 4     |    | <b>17</b> |  [51]    |  [47]  |  [3]    |   |             |
| 5     |    | <b>51</b> |  [88]    |  [10]  |  [2]    |   |             |
| 6     |    | <b>1</b>  |  [71]    |  [29]  |  |   |             |
| 7     |   | <b>3</b>  |  [>99]  |  |  |   |             |
| 8     |  | <b>6</b>  |  [>99] |  |  |   |             |
| 9     |  | <b>27</b> |  [66]  |  [7] |  [19] |  [7] | Others [0]  |
| 10    |  | <b>94</b> |  [98]  | Others [2]   |  |   |             |

Conditions: Substrate 1 g, Water 4 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> 0.3 g, H<sub>2</sub>SO<sub>4</sub> (H<sup>+</sup>/Ir = 1), P<sub>H<sub>2</sub></sub> = 8 MPa, T = 373 K, t = 4 h.  
 BuT = butanetriol, BuD = butanediol, BuOH = butanol.

# Ir-ReO<sub>x</sub>/SiO<sub>2</sub>上のポリオールの水素化分解 ChemSusChem 5, 1991 (2012)

| Entry | Substrate | Conv. / % | Products [selectivity / %] |            |      |            |             |
|-------|-----------|-----------|----------------------------|------------|------|------------|-------------|
| 1     |           | 26        | [37]                       | [21]       | [20] | [8]        | Others [14] |
| 2     |           | 51        | [73]                       | [12]       | [7]  | Others [7] |             |
| 3     |           | 12        | [97]                       |            |      |            |             |
| 4     |           | 17        | [51]                       |            |      |            |             |
| 5     |           | 51        | [88]                       |            |      |            |             |
| 6     |           | 1         | [71]                       |            |      |            |             |
| 7     |           | 3         | [>99]                      |            |      |            |             |
| 8     |           | 6         | [>99]                      |            |      |            |             |
| 9     |           | 27        | [66]                       | [7]        | [19] | [7]        | Others [0]  |
| 10    |           | 94        | [98]                       | Others [2] |      |            |             |

**反応性高い** (High reactivity) at the top and **反応性低い** (Low reactivity) at the bottom, indicated by a red vertical arrow.

**プロトン攻撃によるC-O切断(酸素への攻撃)ではない** (Not C-O cleavage due to proton attack on oxygen).

**● の炭素周りの込み具合が反応性に影響(炭素原子への攻撃)** (The crowdedness of the carbon environment affects reactivity (attack on carbon atom)).

**OH間の距離** (Distance between OH groups).

**1級の水酸基があると高反応性** (High reactivity if a primary hydroxyl group is present).

Conditions: Substrate 1 g, Water 4 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> 0.3 g, H<sub>2</sub>SO<sub>4</sub> (H<sup>+</sup>/Ir = 1), P<sub>H<sub>2</sub></sub> = 8 MPa, T = 373 K, t = 4 h.  
 BuT = butanetriol, BuD = butanediol, BuOH = butanol.

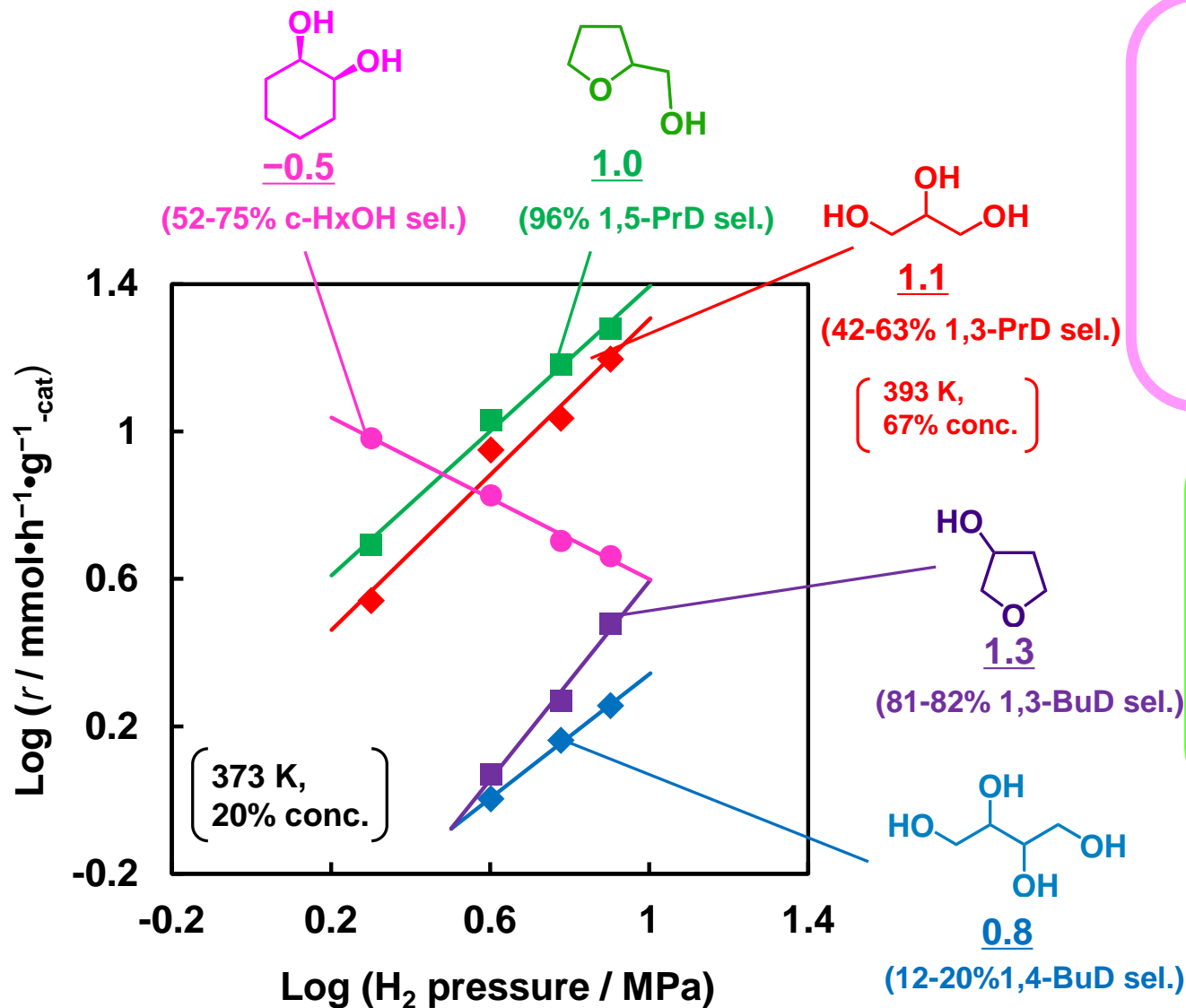
| Entry          | Substrate | Product | <i>t</i> / h | Conv. / % | Selec. / %   | TOF / h <sup>-1</sup> |                 |
|----------------|-----------|---------|--------------|-----------|--------------|-----------------------|-----------------|
| 1              |           |         | 2            | 58.2      | 95.8         | 609                   | Highly reactive |
|                |           |         | 8            | 100       | 82.0         | -                     |                 |
| 2              |           |         | 4            | 40.4      | 87.7         | 186                   | Mildly reactive |
| 3              |           |         | 6            | 23.9      | 81.1         | 96                    |                 |
| 4              |           |         | 6            | 35.0      | 76.4         | 122                   | Non-reactive    |
| 5              |           |         | 6            | 0.0       | 0.0          | 0                     |                 |
| 6              |           |         | 4            | 2.7       | 90.5         | 18                    | Non-reactive    |
| 7 <sup>a</sup> |           |         | 24           | 74.0      | 33.0<br>12.0 | -                     |                 |
| 8              |           |         | 1            | 9.3       | 64.3         | 170                   |                 |

Reaction conditions: substrate 1g, H<sub>2</sub>O 4 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> 150 (<sup>a</sup>300) mg, 373 K, P<sub>H<sub>2</sub></sub> = 8 MPa. <sup>a</sup>H<sub>2</sub>SO<sub>4</sub> (H<sup>+</sup>/Re = 1)

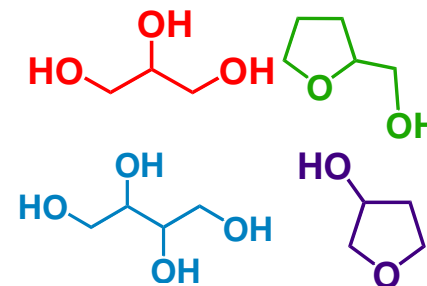
| Entry          | Substrate | Product | <i>t</i> / h | Conv. / % | Selec. / % | TOF / h <sup>-1</sup> |                 |
|----------------|-----------|---------|--------------|-----------|------------|-----------------------|-----------------|
| 1              |           |         | 2            | 58.2      | 95.8       | 609                   | Highly reactive |
|                |           |         | 8            | 100       | 82.0       | -                     |                 |
| 2              |           |         | 4            | 40.4      | 87.7       | 186                   | Mildly reactive |
| 3              |           |         | 6            | 23.9      | 81.1       | 96                    |                 |
| 4              |           |         | 6            | 35.0      | 76.4       | 122                   | Non-reactive    |
| 5              |           |         | 6            | 0.0       | 0.0        | 0                     |                 |
| 6              |           |         | 4            | 2.7       | 90.5       | 18                    |                 |
| 7 <sup>a</sup> |           |         | 1            | 9.5       | 84.5       | 170                   |                 |
| 8              |           |         | 1            | 9.5       | 84.5       | 170                   |                 |

**Ir-ReO<sub>x</sub> はHO-C-C-O- 構造中のC-O結合水素化分解反応を触媒する。**

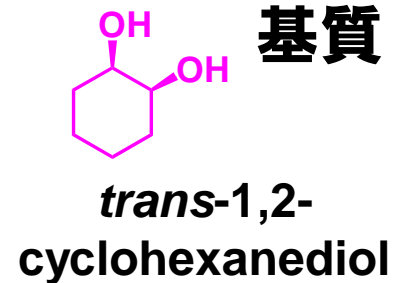
# Ir-ReO<sub>x</sub>触媒上の水素化分解反応キネティクス(水素圧依存性)



ほぼ1次を与える  
基質



マイナス次を  
基質



HO-C-C-O- 構造  
のコンフォメー  
ションに注目



# 基質中構造HO-C-C-O-のC-C周りのコンフォメーション

J. Catal. 294, 171 (2012)

## 水素に対して1次を与える基質

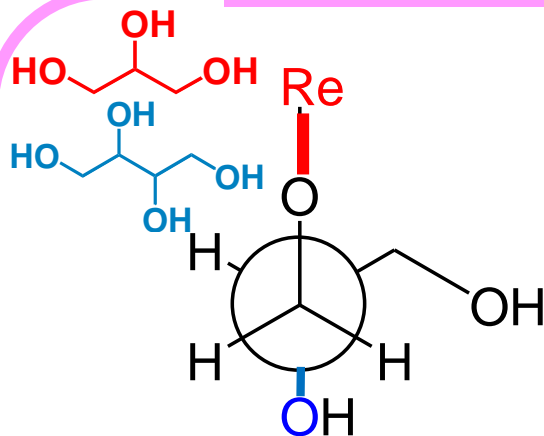
Re



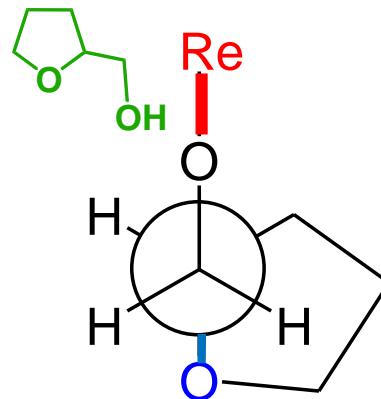
触媒との相互作用  
(Reアルコキシド形成)



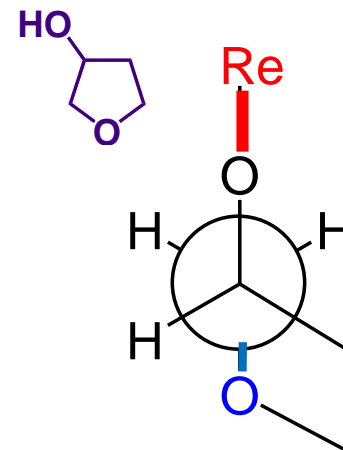
水素化分解される  
C-O結合



Glycerol  
Erythritol



Tetrahydrofurfuryl  
alcohol (THFA)

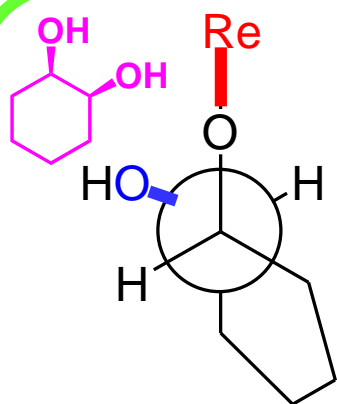


3-Hydroxytetrahydro-  
furan (3-HTHF)

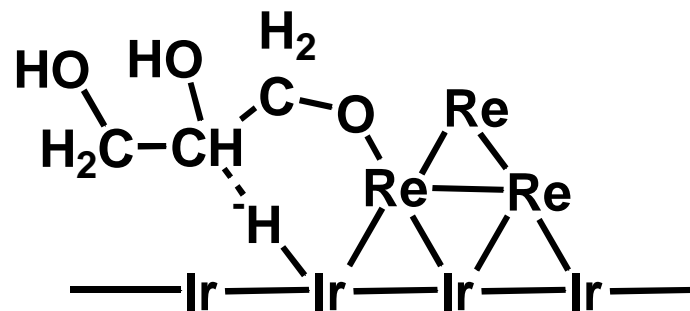
アンチのコンフォメーションが可能

水素に対して  
マイナス次を  
与える基質

アンチのコンフォメーションが不可能



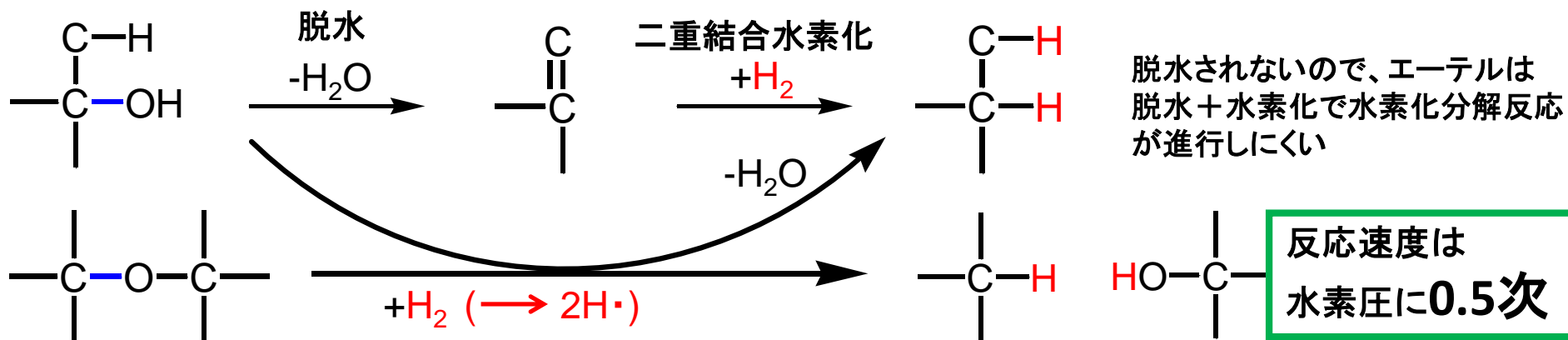
trans-1,2-cyclohexanediol



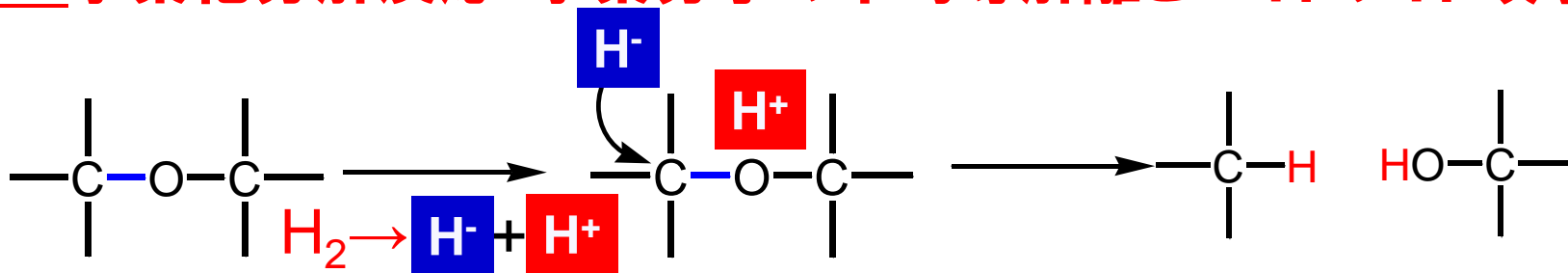
アンチ位置  
S<sub>N</sub>2的なヒドライド攻撃を支持

## 従来型水素化分解反応機構

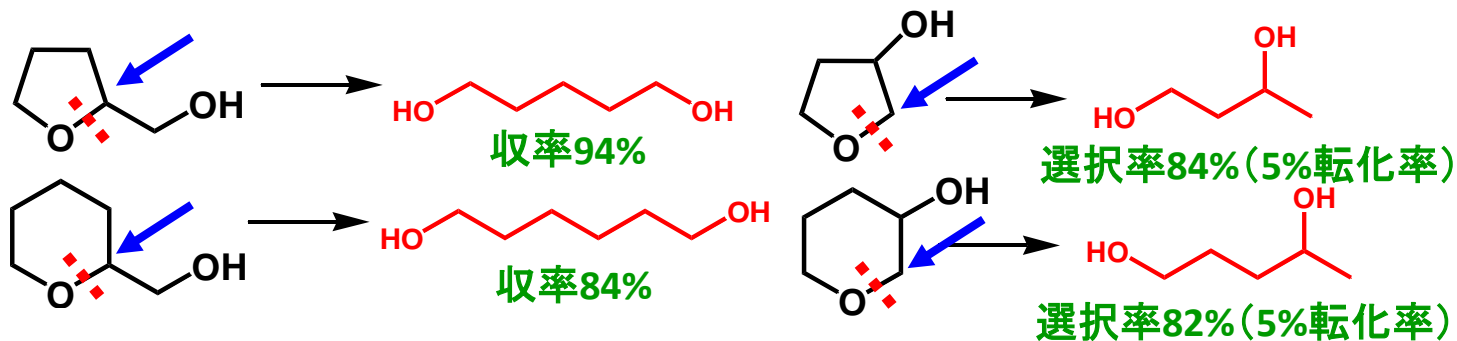
脱水+二重結合水素化 (アルコール) or 水素ラジカル(エーテル or アルコール)



## 新しい水素化分解反応: 水素分子の不均等解離とヒドライド攻撃



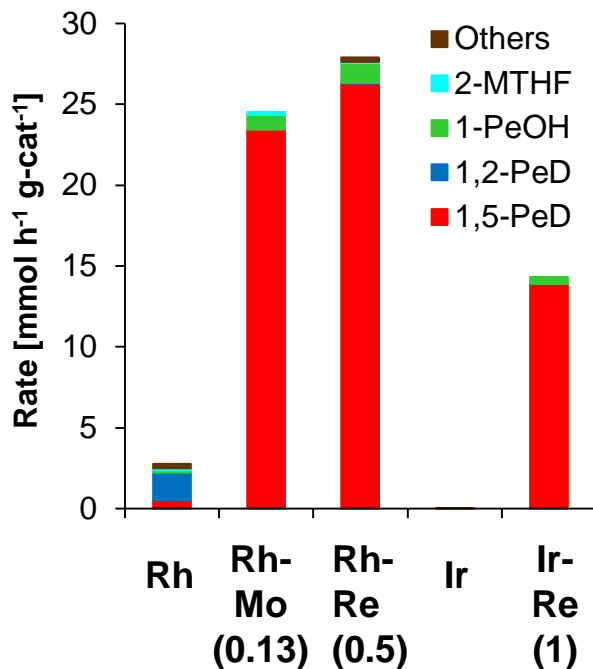
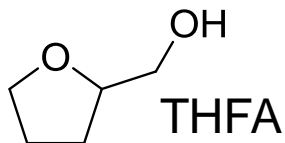
アルコール・エーテル両方に適応可能。水酸基と触媒との相互作用によりヒドライドの攻撃位置を制限し、高選択性を実現



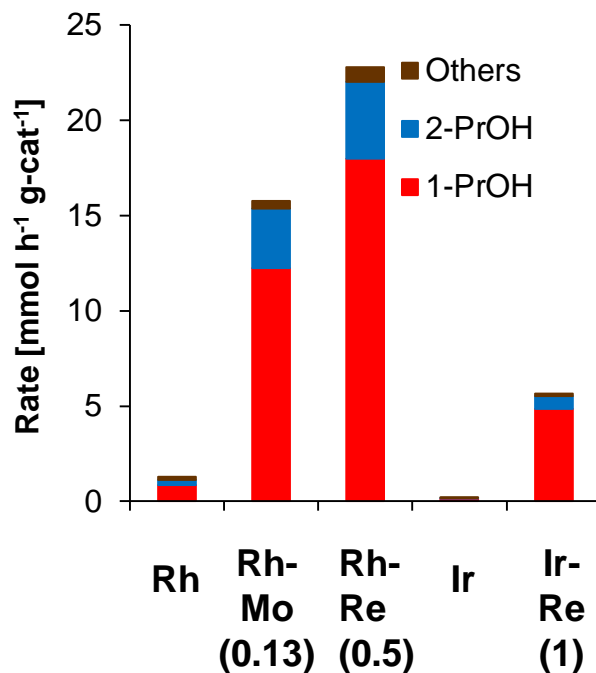
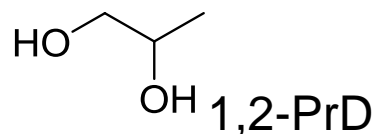
反応速度は水素圧に**1次**

# Hydrogenolysis of THFA, 1,2-PrD, and Glycerol

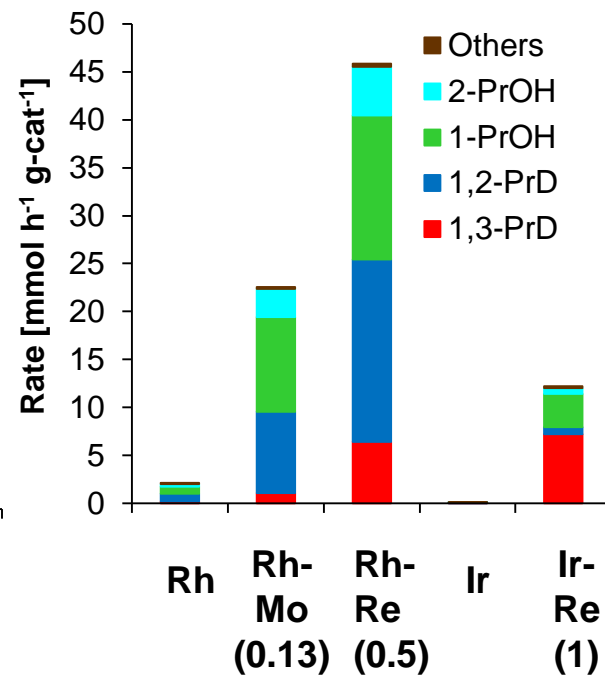
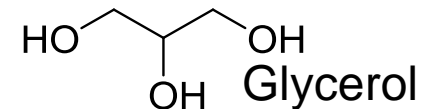
## Single OH group



## Double OH group



## Triple OH group



Hydrogenolysis activity order using these substrates tends to be similar.

→ Rh-Re > Rh-Mo > Ir-Re

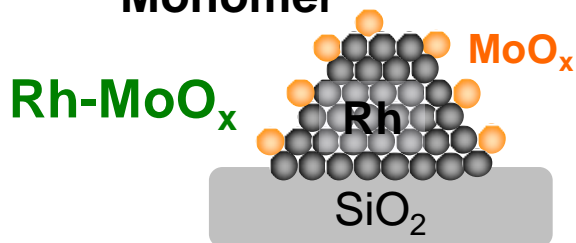
Selectivity is strongly influenced by the number of OH groups.

→ Ir-Re > Rh-Re > Rh-Mo

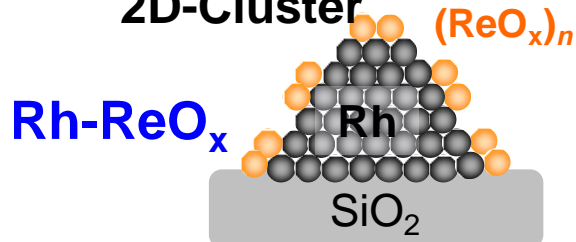
# 触媒特性と構造の関係

Chem. Commun. 2009, J. Catal. 2009  
 Chem. Lett. 2009, Appl. Catal. B 2010  
 ChemCatChem 2010, J. Catal. 2010  
 ChemSusChem 2010, J. Catal. 2011  
 Appl. Catal. B 2011,  
 Appl. Catal. B 2012

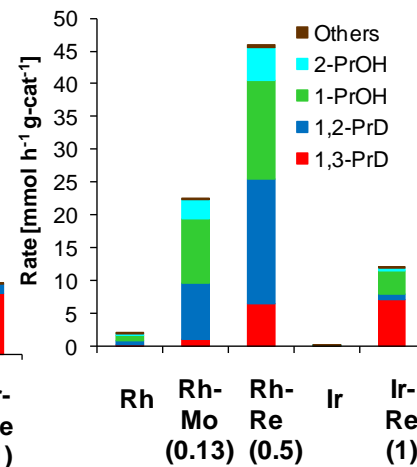
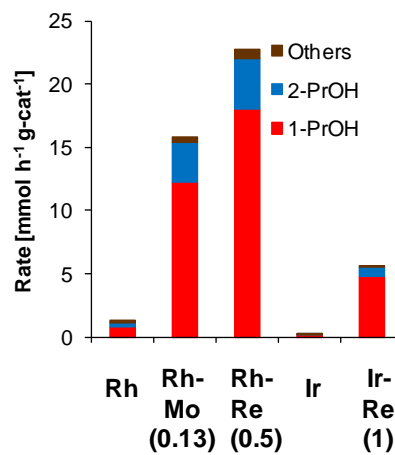
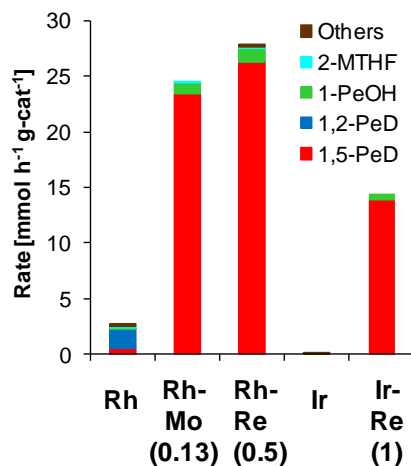
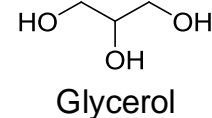
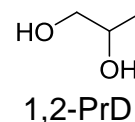
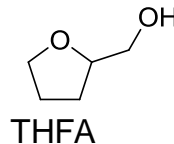
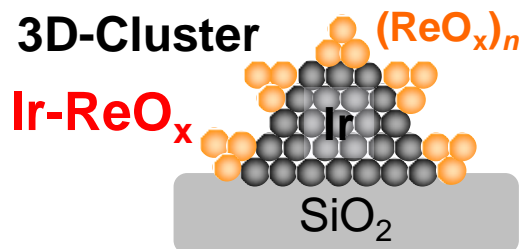
## Monomer



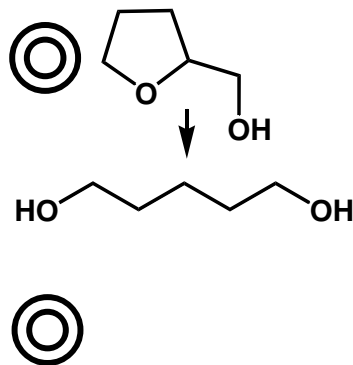
## 2D-Cluster



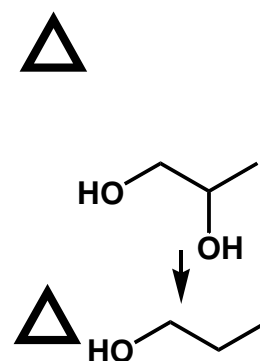
## 3D-Cluster



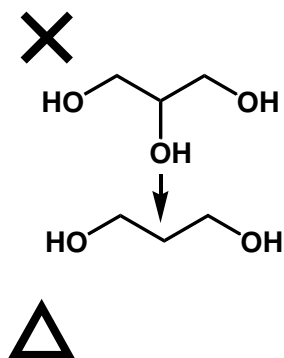
## THFA



## 1,2-PrD



## Glycerol

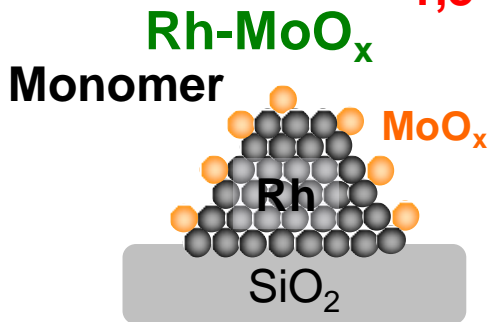
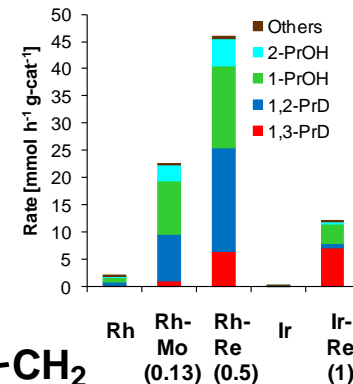
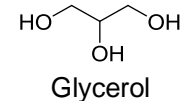


水素化分解選択率は修飾剤の構造の影響を受ける。  
 monomer, 2-D or 3-D clusters



3-D cluster が高選択率に有効

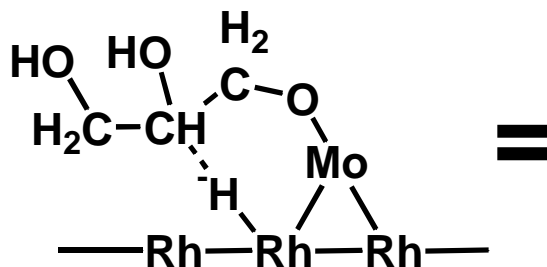
# グリセリン水素化分解選択率と構造の相関の解釈 (遷移状態)



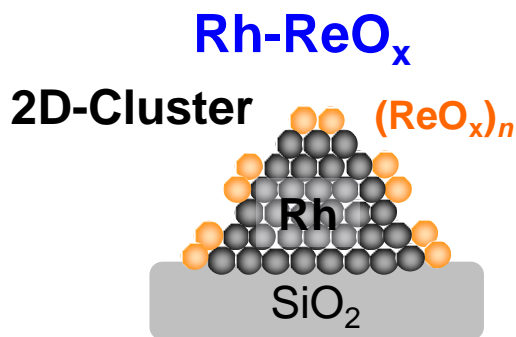
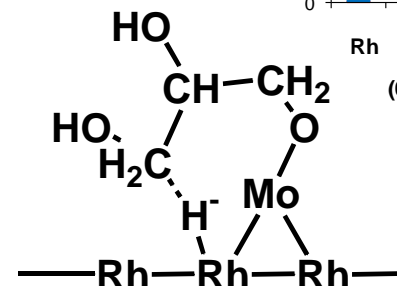
1,3-PrD 選択率

低

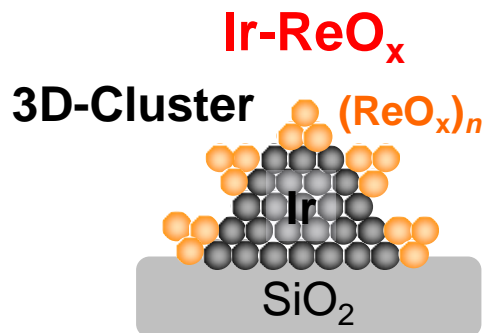
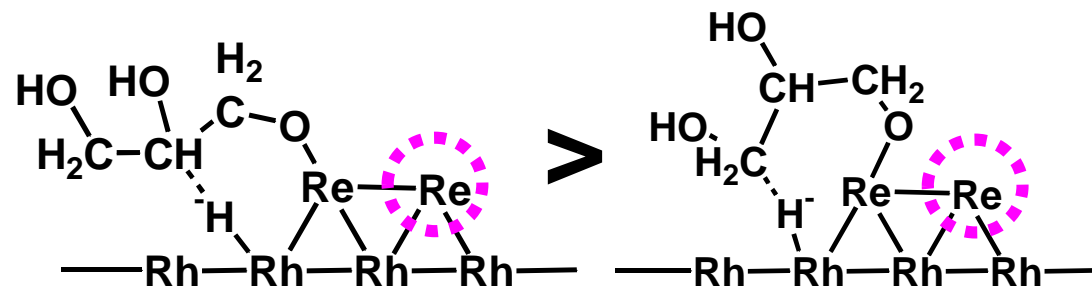
6員環  
遷移状態  
to 1,3-PrD



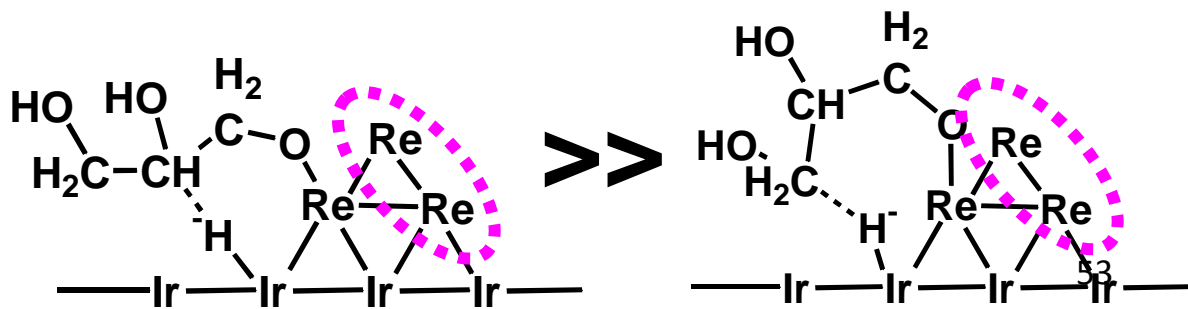
7員環  
遷移状態  
to 1,2-PrD



中



高



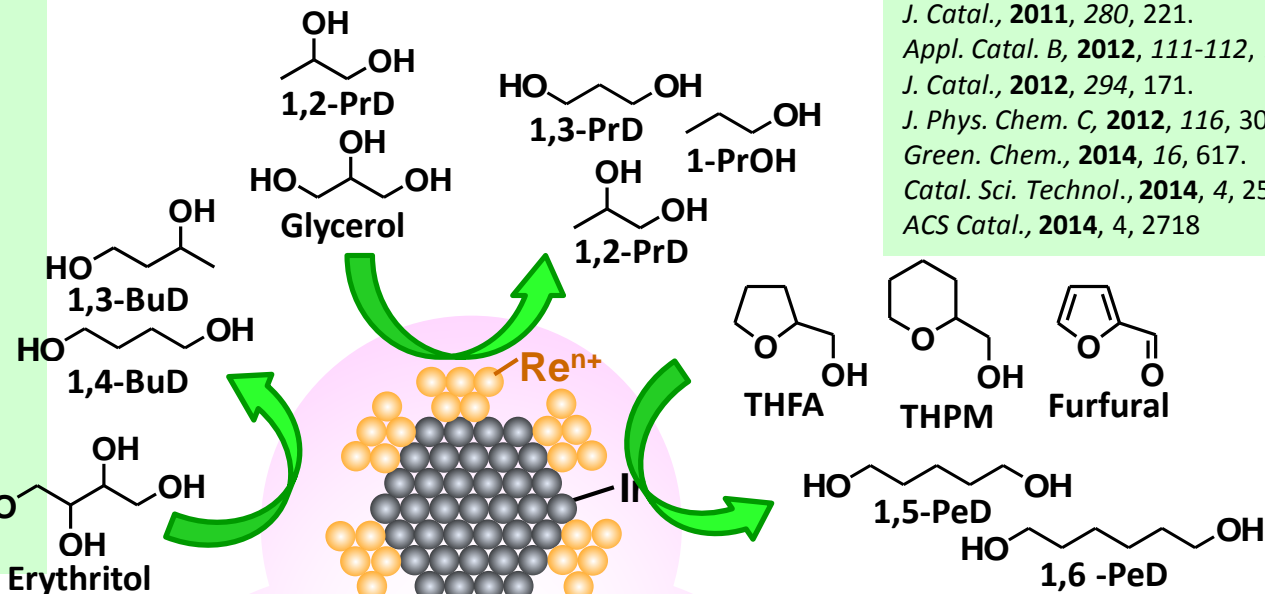
# Selective hydrogenolysis

## Glycerol

*Chem. Lett.*, **2009**, 38, 540.  
*Appl. Catal. B*, **2010**, 94, 318.  
*ChemSusChem*, **2010**, 3, 728.  
*J. Catal.*, **2010**, 272, 191.  
*Appl. Catal. B*, **2011**, 105, 117  
*Appl. Catal. A*, **2012**, 433-434, 128.  
*J. Phys. Chem. C*, **2012**, 195, 23503.  
*ChemSusChem*, **2012**, 5, 1991.  
*Appl. Catal. A*, **2013**, 468, 418.  
*J. Mol. Catal. A*, **2014**, 2, 6688.

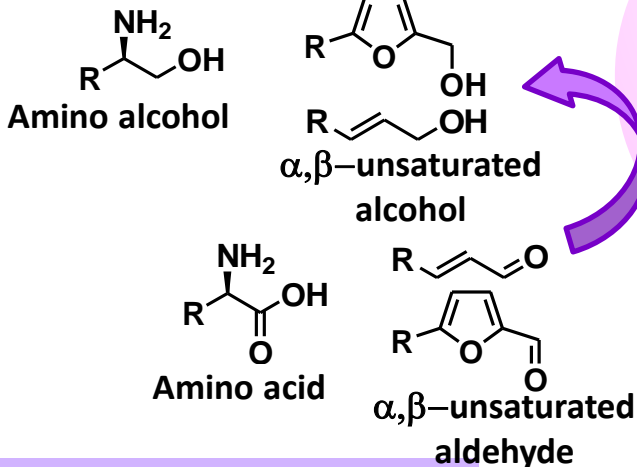
## Erythritol, Anhydroerythritol

*ChemSusChem* **2012**, 5, 1991.  
*ChemSusChem* **2014**, 7, 2185.  
*Angew. Chem. Int. Ed.* **2015**, 54, 1897

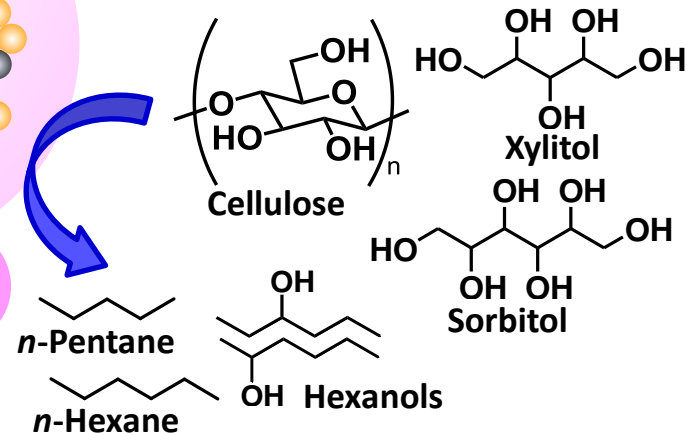


*Chem. Commun.*, **2009**, 2035.  
*J. Catal.*, **2009**, 267, 89.  
*ChemCatChem*, **2010**, 2, 547.  
*J. Catal.*, **2011**, 280, 221.  
*Appl. Catal. B*, **2012**, 111-112, 27.  
*J. Catal.*, **2012**, 294, 171.  
*J. Phys. Chem. C*, **2012**, 116, 3079.  
*Green. Chem.*, **2014**, 16, 617.  
*Catal. Sci. Technol.*, **2014**, 4, 2535.  
*ACS Catal.*, **2014**, 4, 2718

## Selective hydrogenation



## Complete hydrogenolysis



## M+MO<sub>x</sub> catalysts

*Catal. Surv. Asia*, **2011**, 15, 111.  
*Catal. Sci. Technol.*, **2011**, 1, 179.  
*ACS Catal.*, **2013**, 3, 2655.  
*J. Mater. Chem. A*, **2014**, 4, 6688.  
*Top. Curr. Chem.*, **2014**, 353, 127  
*Chem. Rec.*, **2014**, 14, 104  
*ChemSusChem*, **2015**, 8, 1114

*ChemSusChem* **2013**, 6, 613.  
*ACS Sustainable Chem. Eng.* **2014**, 2, 1819.  
*ChemSusChem*, **2015**, 8, 628

*Chem. Commun.* **2014**, 50, 6656.  
*Chem. Commun.* **2013**, 49, 7034.  
*Chem. Eur. J.* **2015**, 21, 3097.  
*ChemSusChem* **2015**, 8, 1170.