CO_2 水素化の選択性の制御因子について

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第5回SPring-8先端放射光技術による化学イノベーション研究会
/ 第62回SPring-8先端利用技術ワークショップ
「先端放射光分析が拓く低炭素社会実現のための化学イノベーション」
2021/7/9

In May 2019, Tokyo announced that it will take responsibility as a global megacity, and pursuing the 1.5℃ goal, realize a "Zero Emission Tokyo" by 2050, that contributes to the world's net zero emissions.

Zero Emission Tokyo

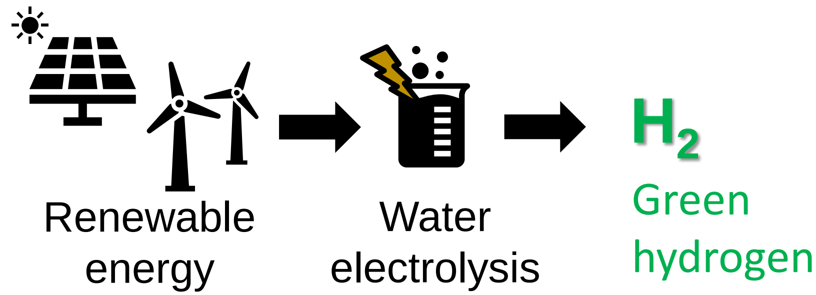
A decarbonization strategy to realize a Tokyo that serves as a pioneer for our brilliant future

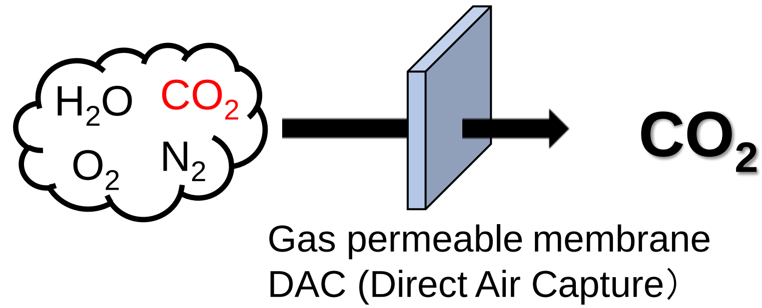
Zero Emission Tokyo Strategy

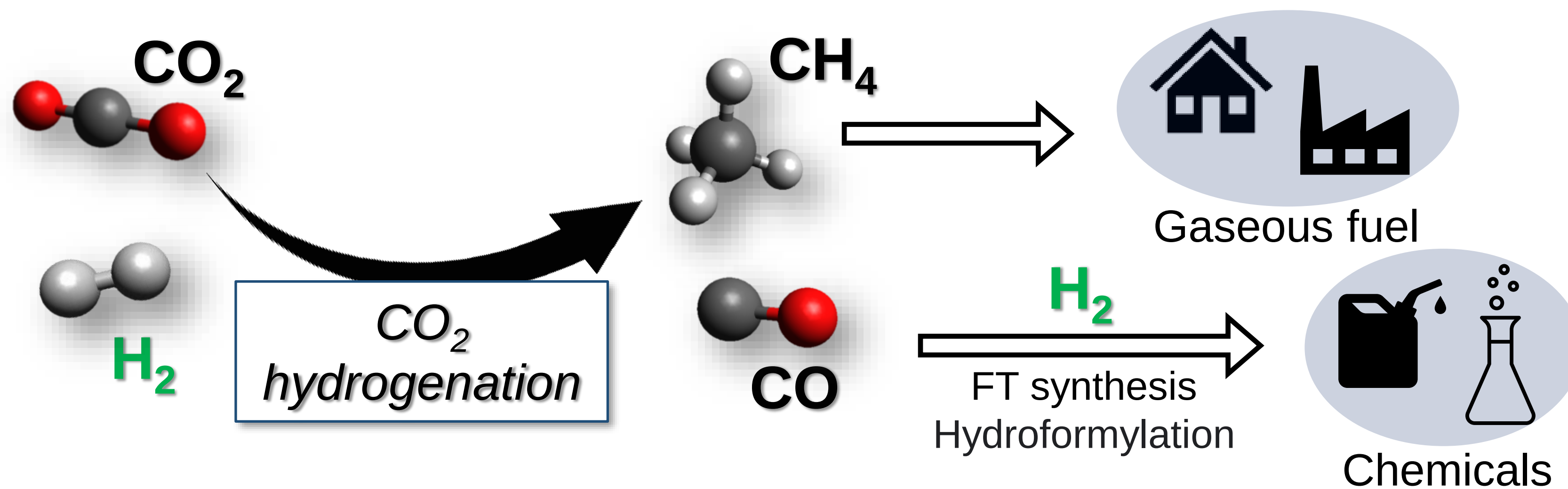
"Decarbonization"

東京都においても様々な
取り組みを推進している

Utilization of CO_2 as a carbon source







Sabatier reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H_{298K} = -165 \text{ kJ mol}^{-1}$$

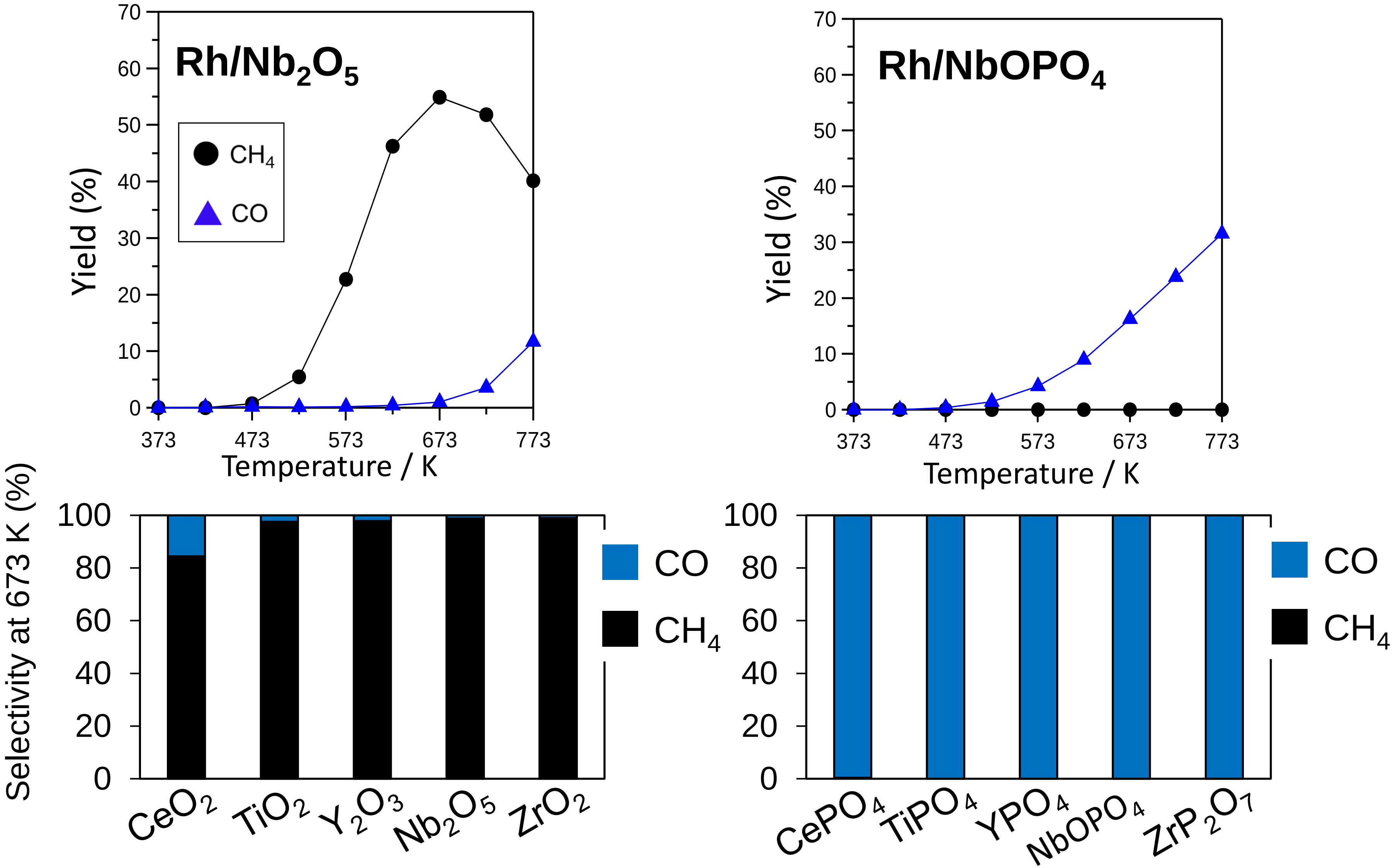
Reverse water gas shift (r-WGS)

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta H_{298K} = 41 \text{ kJ mol}^{-1}$$

Selectivity of CO_2 hydrogenation

Catalyst	Conditions	CH_4 sel./ %	Ref.
0.5wt% Rh/TiO_2	CO_2/H_2=1/4	98% @623K	P. Panagiotopoulou, *Appl. Catal. A*, **2017**, 542, 63
1wt% Rh/Al_2O_3	CO_2/H_2=1/4 0.2 MPa	100% @398K	C. Swalus et al., *Appl. Catal. B*, **2012**, 125, 41
3wt% Rh/CeO_2	CO_2/H_2=1/4 0.2 MPa	90% @625K	N. M. Martin et al., *Catal. Sci. Technol.*, **2019**, 9, 1644.
$LaNiO_3$	CO_2/H_2=1/2	92% @623K	J. G. Chen et al., *Chem. Commun.*, **2018**, *54*, 7354
$LaFe_{0.5}Ni_{0.5}O_3$	CO_2/H_2=1/2	3.2% @623K	
Rh/Al_2O_3	CO_2/H_2=1/1	96% @623K	U. Bentrup et al., *ACS Catal.*, **2016**, *6*, 6275
RhK/Al_2O_3	CO_2/H_2=1/1	53% @623K	
RhNiK/Al_2O_3	CO_2/H_2=1/1	23% @623K	

選択性の制御 ➡ 複数種の金属成分
アルカリ金属での修飾



Manuscript in preparation

Pretreatment conditions : H_2 red. at 673 K for 1 h (H_2 / He =10 / 40 mL min^{-1})

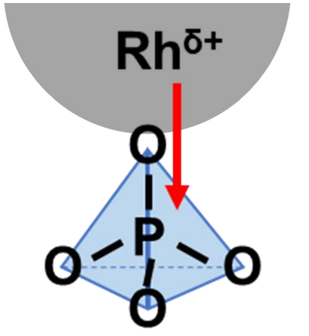
Reaction conditions : CO_2 / H_2 = 10 / 40 mL min^{-1}, He balance, GHSV = 60000 mL g^{-1} h^{-1}

Effect of phosphorus

✓ The electron-withdrawing effect of PO_4 unit

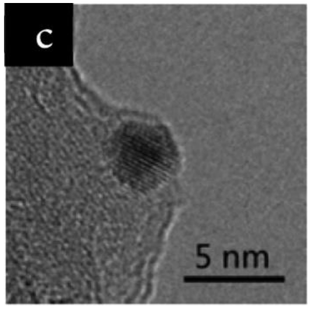
→Decrease in back-donation from the Rh d orbitals to the antibonding π* orbitals of adsorbed CO

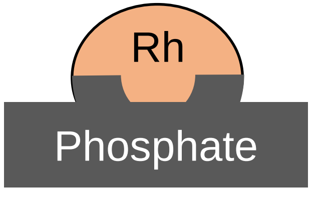
M. Machida et al., *J. Phys. Chem. C* **2015**, *119*, 11653–11661



✓ The strong metal support interactions(SMSIs) between metal NPs and the phosphate support

L. Wang et al., *ChemSusChem* **2020**, *13*, 6300–6306
H. Tang et al., *J. Am. Chem. Soc.* **2016**, *138*, 56–59

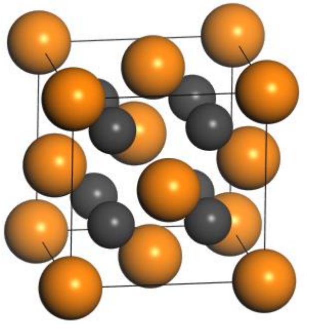




✓ Formation of metal phosphide (ex. Rh_2P)

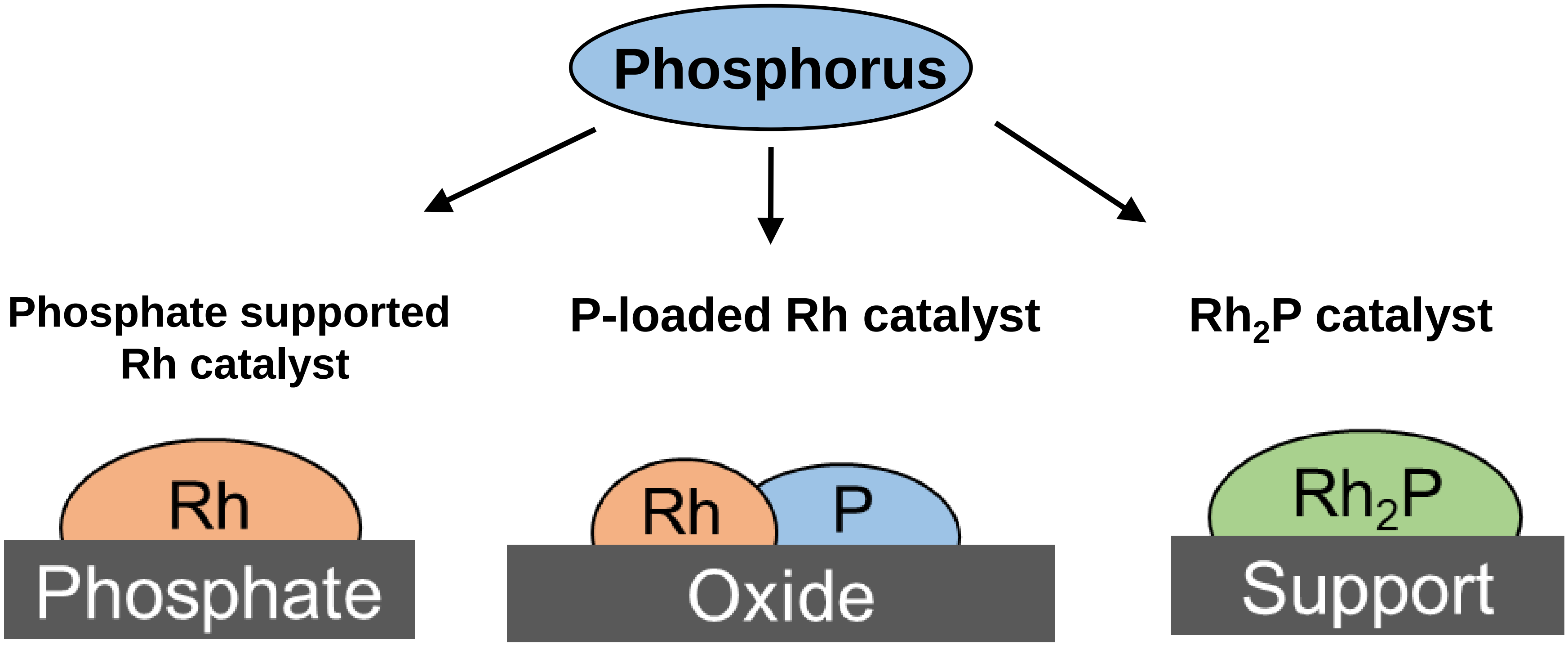
→Rh site with positive charge

J.R. Hayes et al., *J. Catal.* **2010**, *276*, 249–258
Y. Kanda et al., *Chem. Lett.* **2019**, *48*, 471–474



Rh_2P

Preparation of Rh-based catalysts



To reveal the structure and electronic state of active Rh species,

- Phosphate supported Rh, P-loaded Rh, supported Rh_2P catalysts were prepared.
- The structure and electronic state of Rh species were characterized.
- The relationship between catalytic performance and the structure and electronic state of Rh species was investigated.

Preparation of supported Rh catalyst

Impregnation method

$RhCl_3$ aq.

← Support

← Distilled water

← ($NH_4H_2PO_4$)

Impregnated at 353 K for 2 h

Dried at 353 K overnight

Calcined at 773 K for 3 h

→ **Rh / Support**

Rh-xP / Support

x indicates the molar ratio of P to Rh

Support		
TiO_2	JRC-TIO-15	Calcined at 773 K for 3 h
Nb_2O_5	JRC-NBO-1	
ZrO_2	JRC-ZRO-7	
CeO_2	JRC-CEO-2	
SiO_2	JRC-SIO-10	
$NbOPO_4$	CBMM-40	
$CePO_4$	wako	
ZrP_2O_7	Precipitation method	
TiP_2O_7	Stirring and calcining TiO_2 and H_3PO_4	

I.-C. Marcu, et al., *J Mol Catal A: Chem* **2003**, 203, 241–250.

Preparation of supported Rh_2P catalysts

$RhCl_3$ aq.

← Oleylamine

← 1-Octadecene

Heated at 383 K under vac. for 3 h

Aged at 503 K under Ar flow for 1.5 h

← Trioctylphosphine

Heated at 623 K under Ar for 3 h

Cooled down at r.t.

Centrifuged (Toluene:2-propanol =1:5, volume ratio)

Rh_2P NPs

← Hexane:Toluene=1:3, volume ratio

← Support

Stirred at r.t. for 12 h

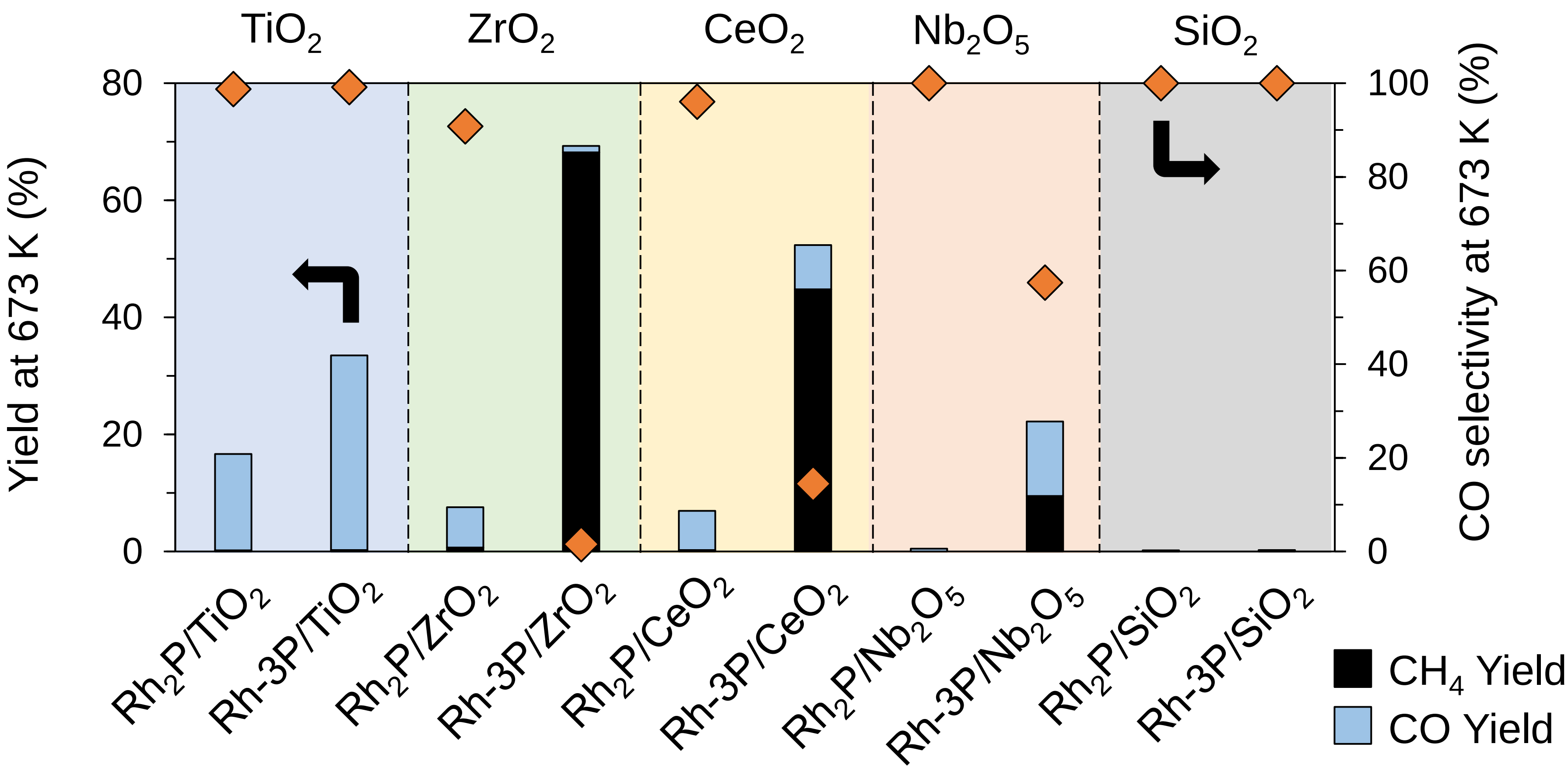
Centrifuged with hexane

Dried at r.t. under vac. overnight

1 wt% Rh_2P/Support

Samuel I. Mutinda et al., *J. Mater. Chem. A*, **2018**, *6*, 12142-12152.

Effect of supports



✓ Rh_2P/TiO_2 and $Rh\text{-}3P/TiO_2$ showed a high CO yield and selectivity.

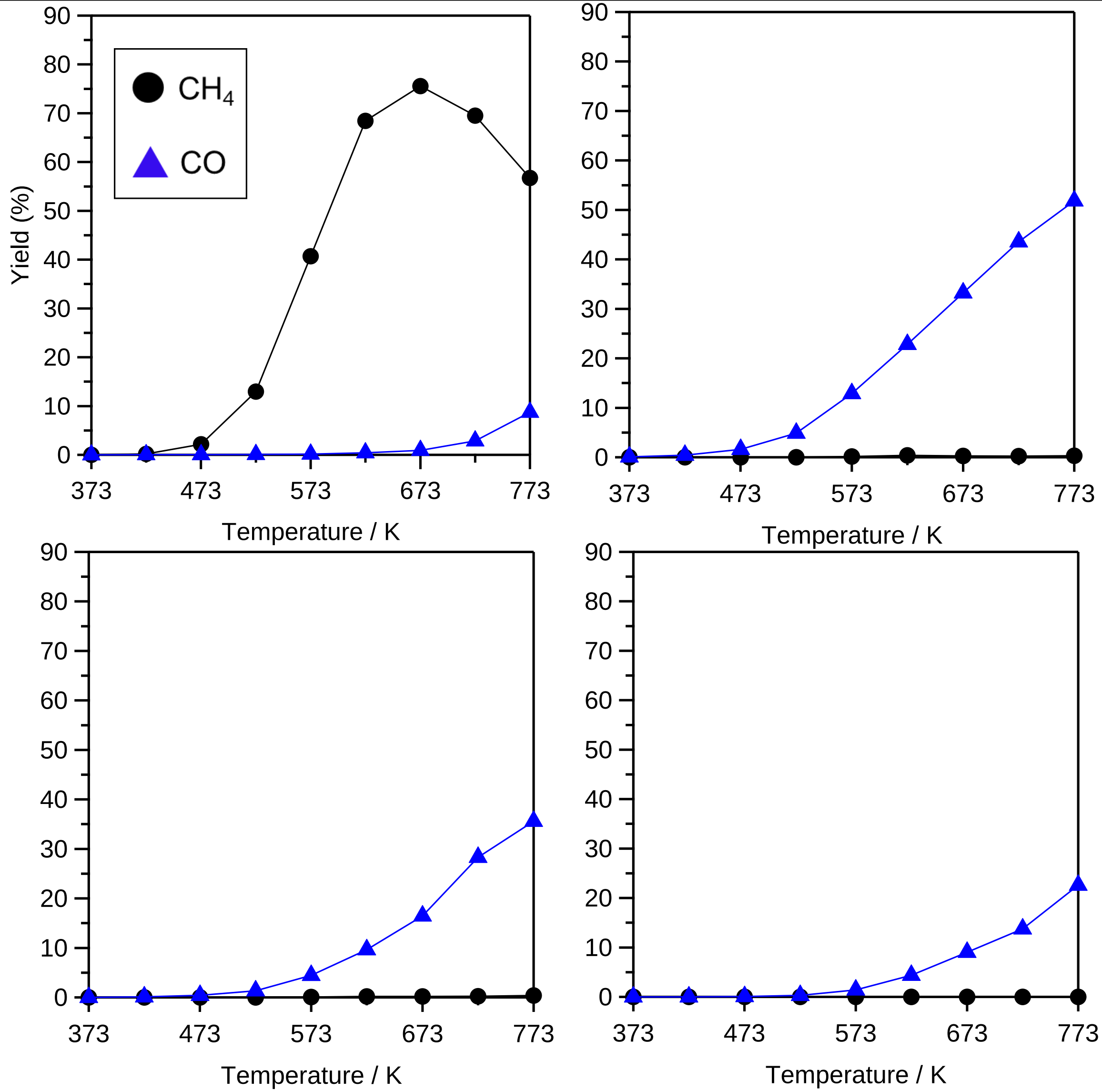
Pretreatment conditions : H_2 red. at 673 K for 1 h (H_2 / He =10 / 40 mL min^{-1})
Reaction conditions : CO_2 / H_2 / N_2 / He = 10 / 40 / 5 / 45 mL min^{-1}
Catalyst amount : 100 mg, Loading amount : 1 wt%

Rh/TiO_2

$Rh\text{-}3P/TiO_2$ (P/Rh=3/1)

Rh_2P/TiO_2

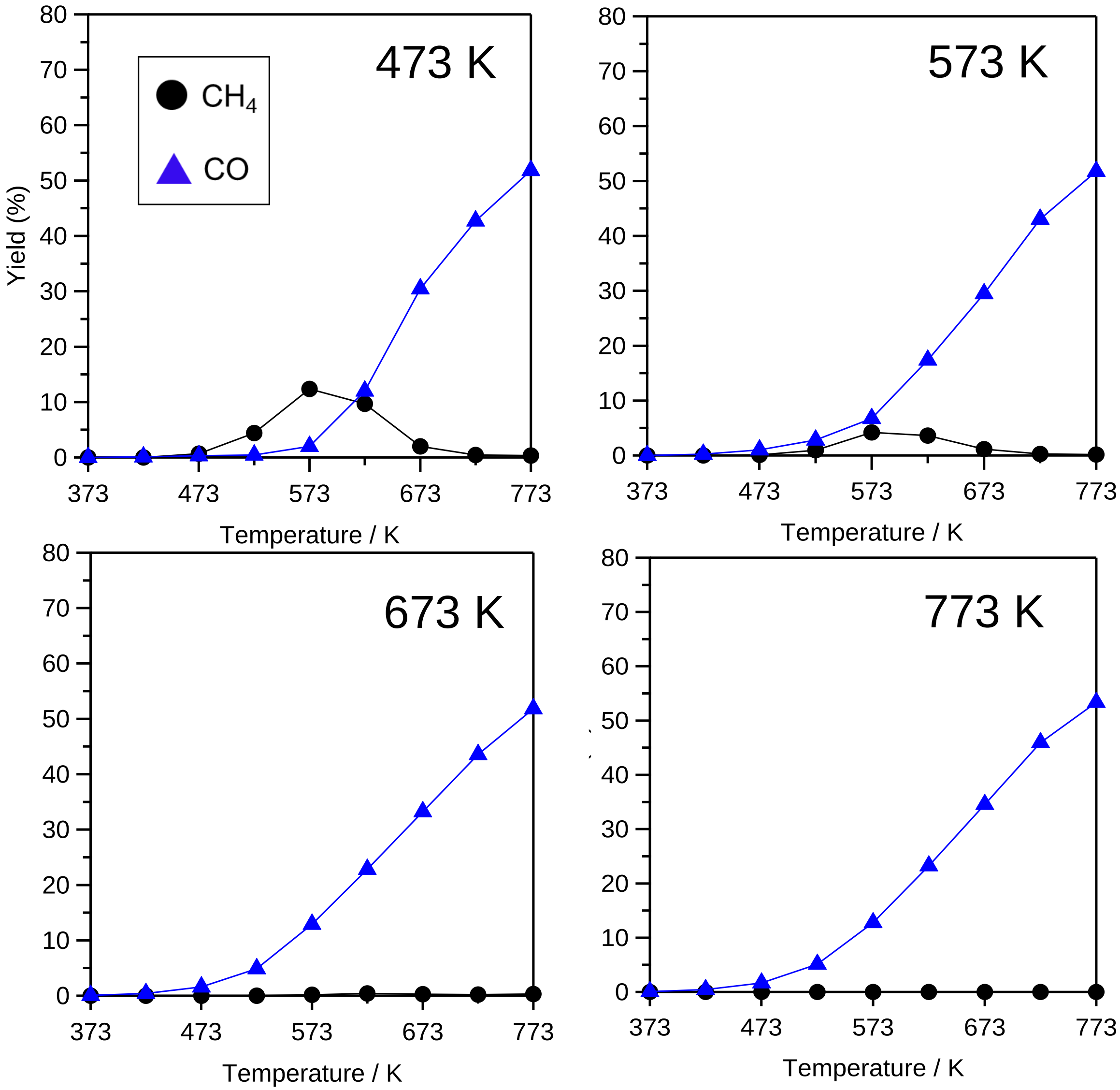
Rh/TiP_2O_7



Pretreatment conditions : H_2 red. at 673 K for 1 h (H_2 / He =10 / 40 mL min^{-1})
Reaction conditions : CO_2 / H_2 / N_2 / He = 10 / 40 / 5 / 45 mL min^{-1}
Catalyst amount : 100 mg, Loading amount : 1 wt%

Effect of reduction pretreatment temperature

Rh-3P/TiO_2

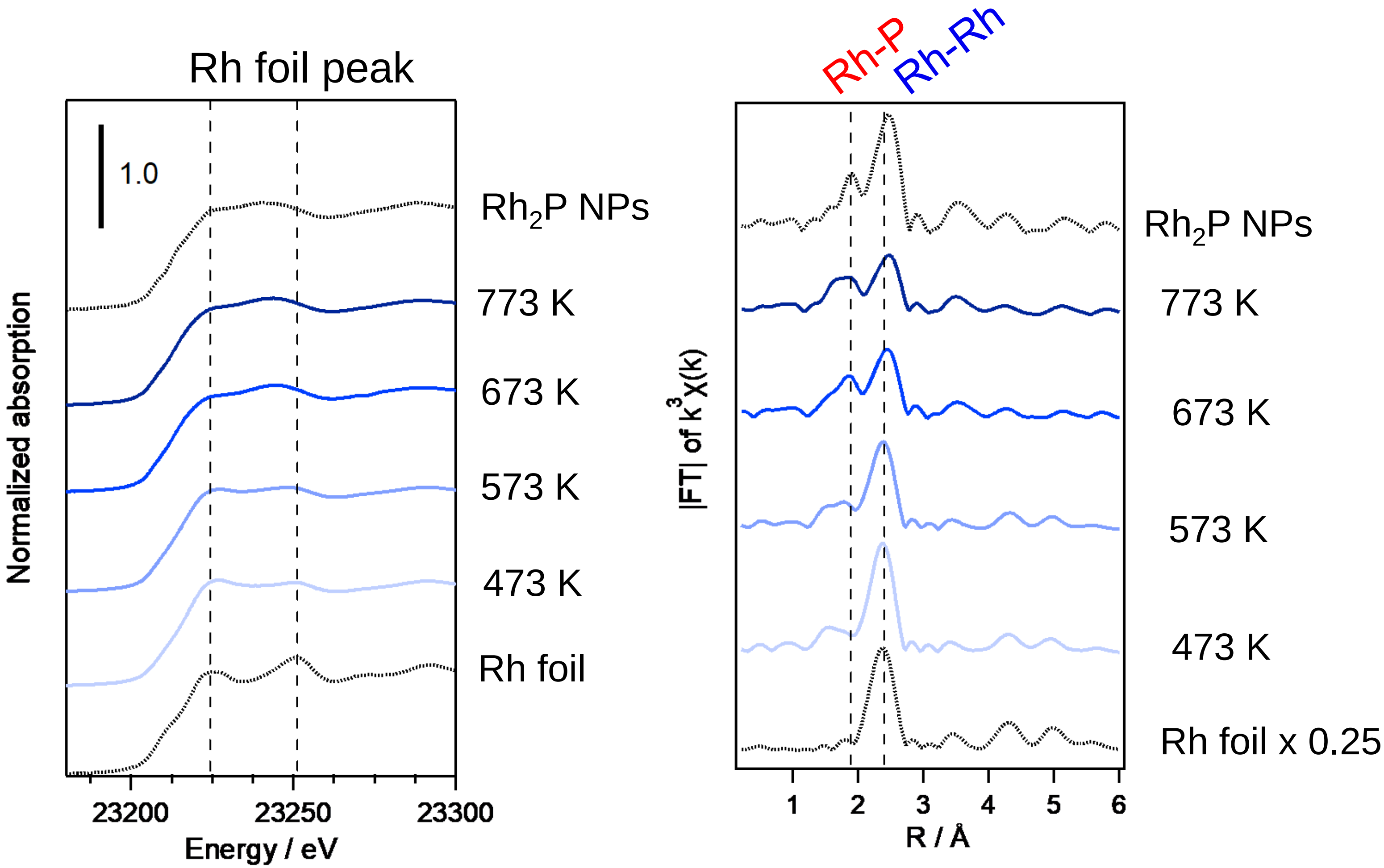


Pretreatment conditions : H_2 red. for 1 h (H_2 / He =10 / 40 mL min^{-1})

Reaction conditions : CO_2 / H_2 / N_2 / He = 10 / 40 / 5 / 45 mL min^{-1}

Catalyst amount : 100 mg, Loading amount : 1 wt%

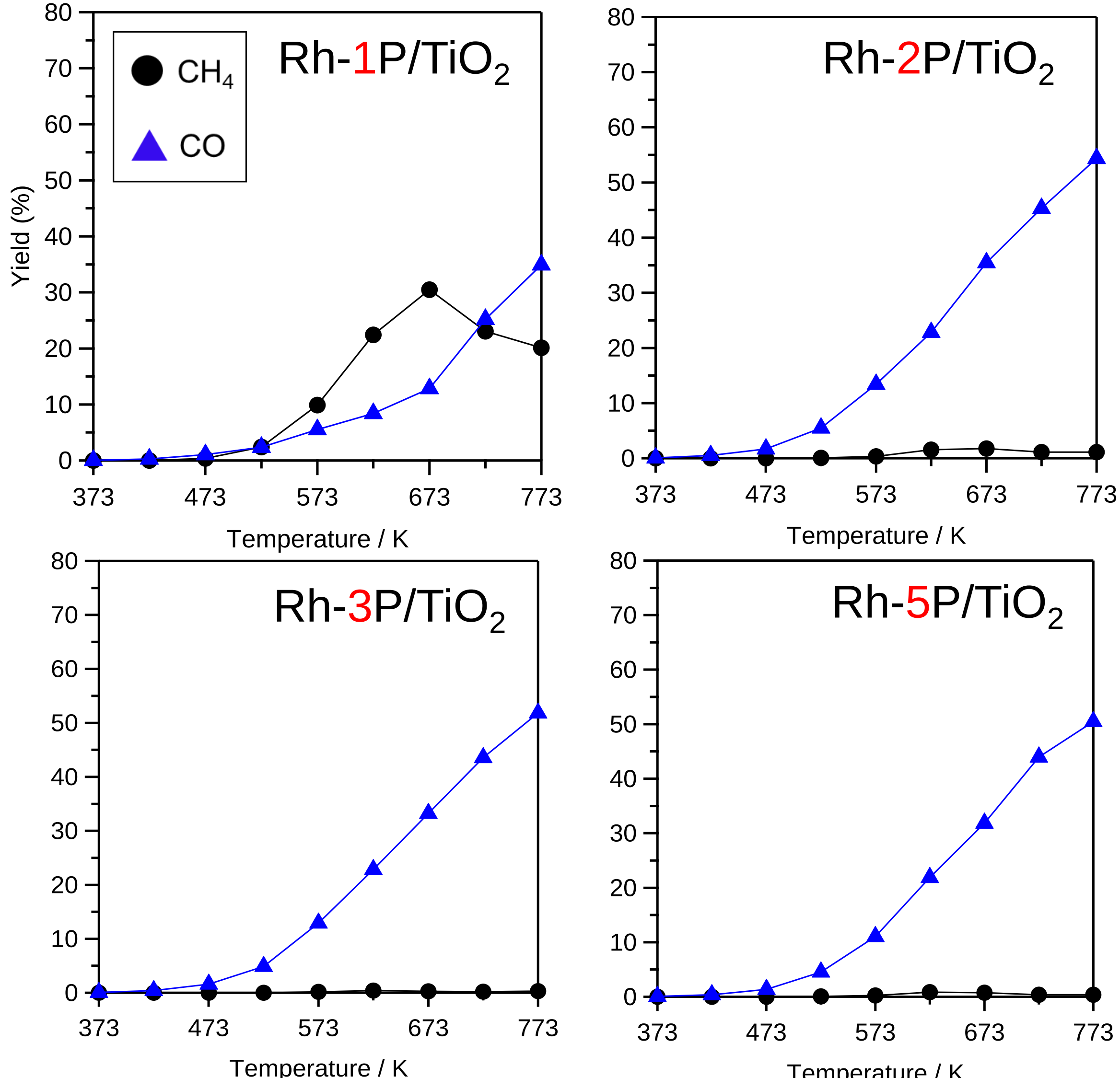
Effect of reduction pretreatment temperature



- ✓ Rh-3P/TiO_2 reduced over 673K showed change in XANES spectral shape from Rh foil to Rh_2P.
- ✓ The higher the reduction temperature, the increasing the Rh-P bond and decreasing the Rh-Rh bond from Fourier transformed EXAFS oscillation.

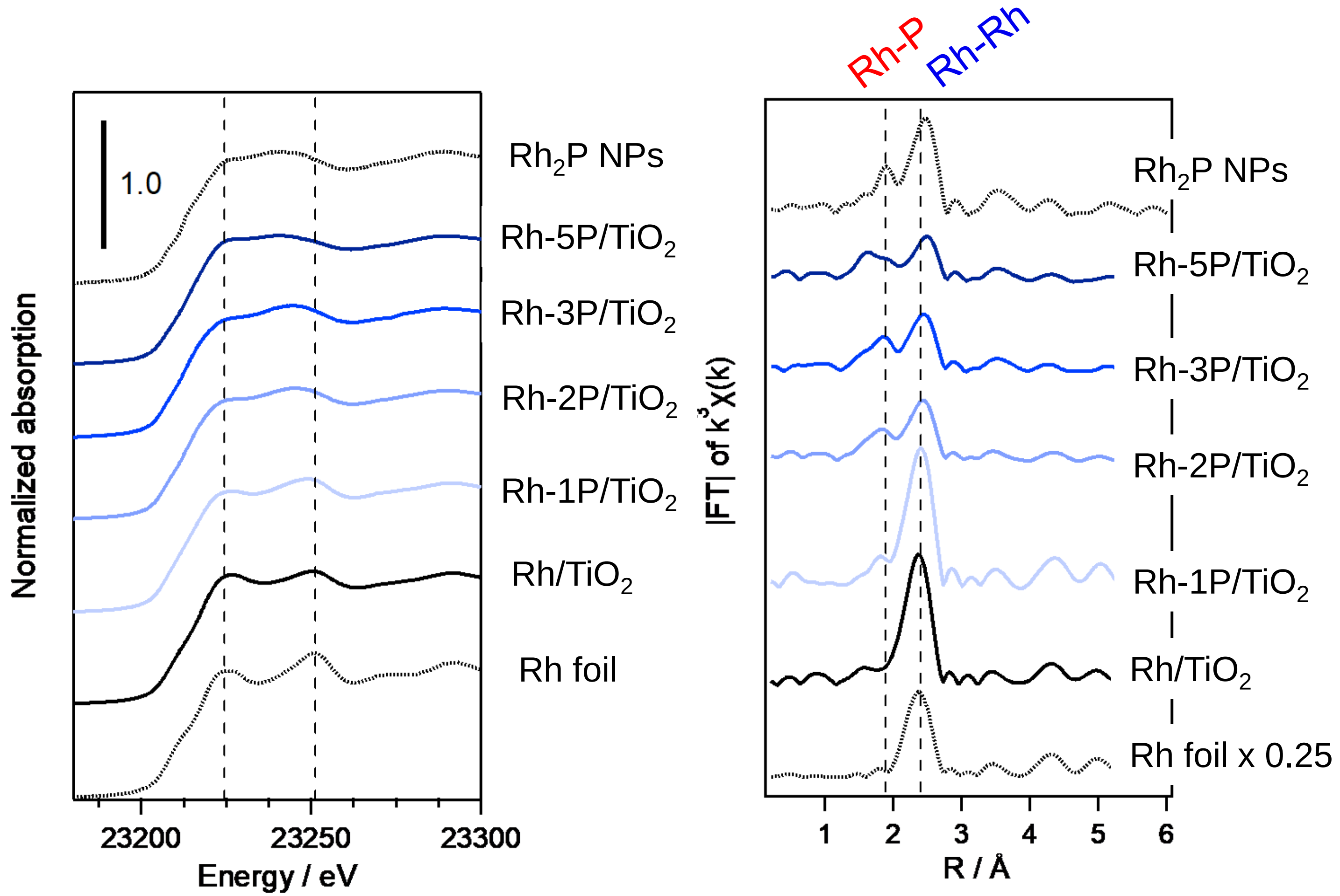
Measured at SPring-8 BL01B1, Loading amount : 5 wt%

Effect of P/Rh ratio of Rh-P/TiO_2



Pretreatment conditions : H_2 red. at 673 K for 1 h (H_2 / He =10 / 40 mL min^{-1})
Reaction conditions : CO_2 / H_2 / N_2 / He = 10 / 40 / 5 / 45 mL min^{-1}
Catalyst amount : 100 mg, Loading amount : 1 wt%

Effect of P/Rh ratio of Rh-P/TiO_2

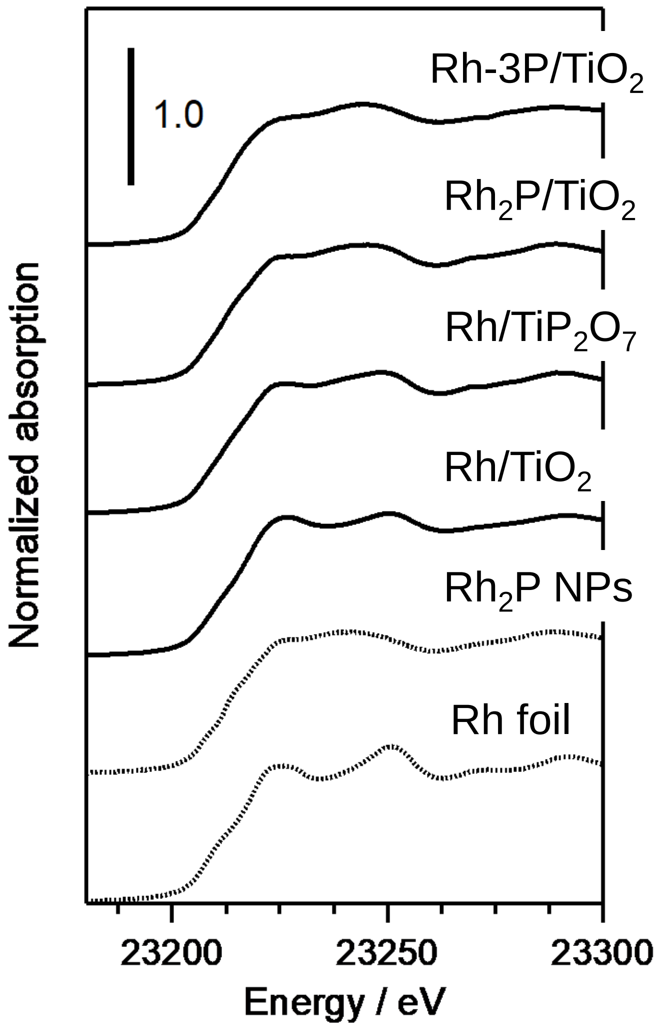


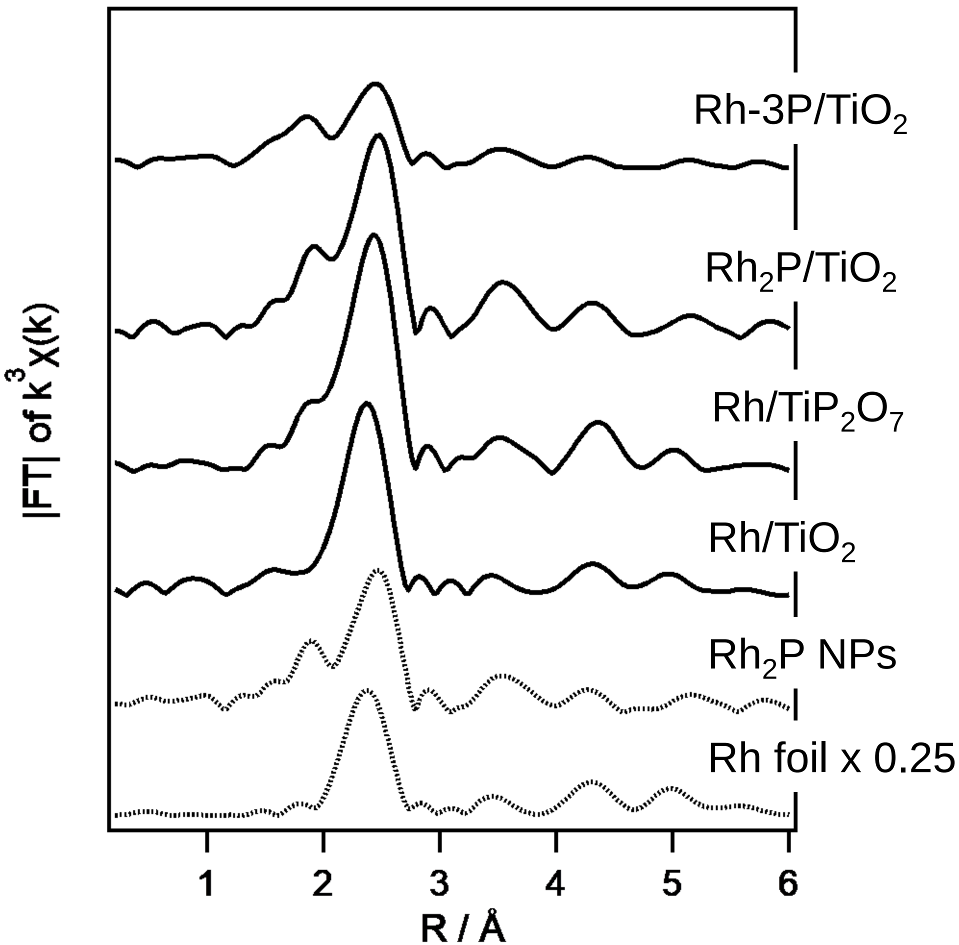
✓ Catalysts with P/Rh molar ratio of 2 or more showed change in XANES spectral shape from Rh foil to Rh_2P and the Rh-P bond was confirmed from Fourier transformed EXAFS oscillation.

S. Liu, et al., *J. Mater. Chem. A* **2020**, *8*, 25768–25779.

Measured at SPring-8 BL01B1, Loading amount : 5 wt%

Differences of depending on the method of adding phosphorus

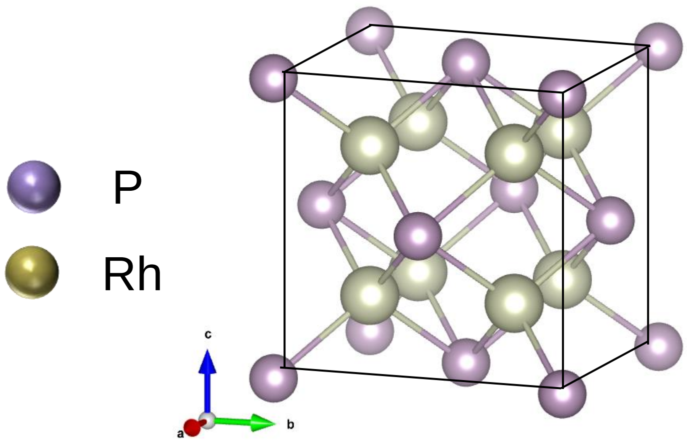




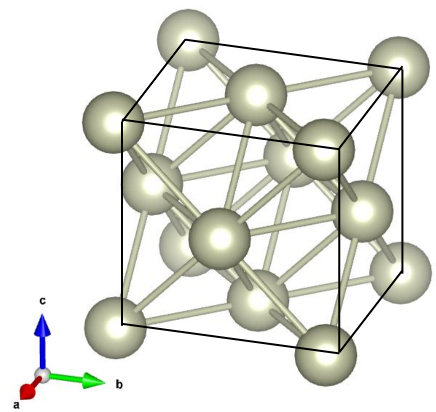
Measured at SPring-8 BL01B1, Loading amount : 5 wt%

Structure: Rh_2P and Rh metal

Rh_2P structure : cubic



Rh structure : cubic

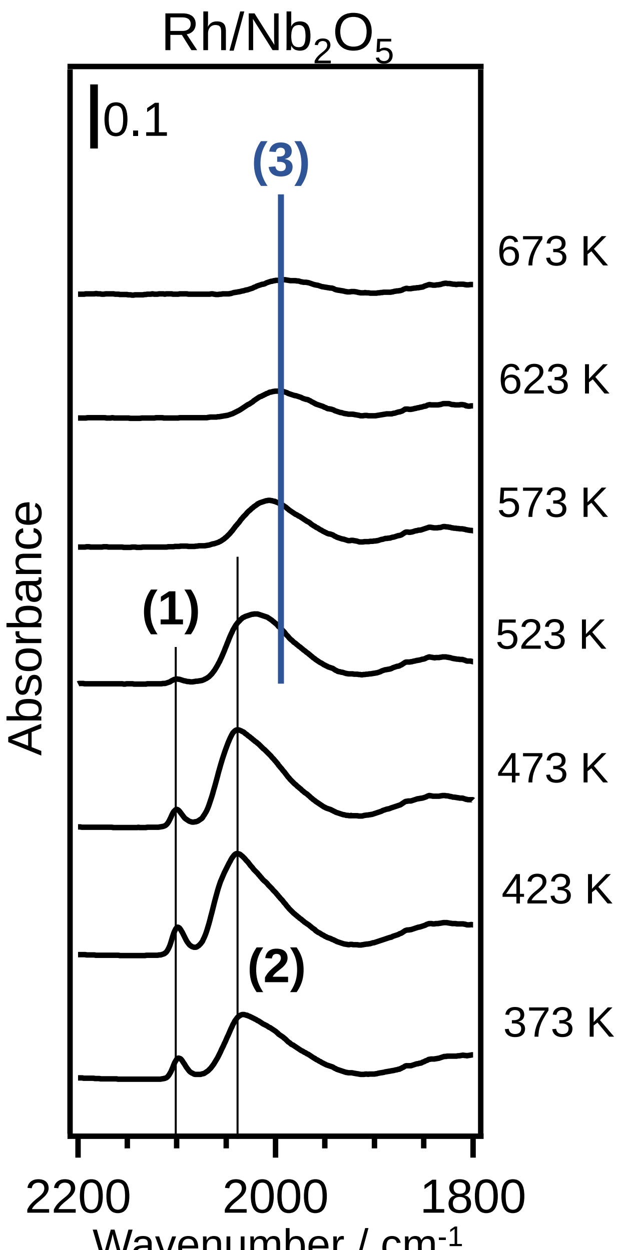


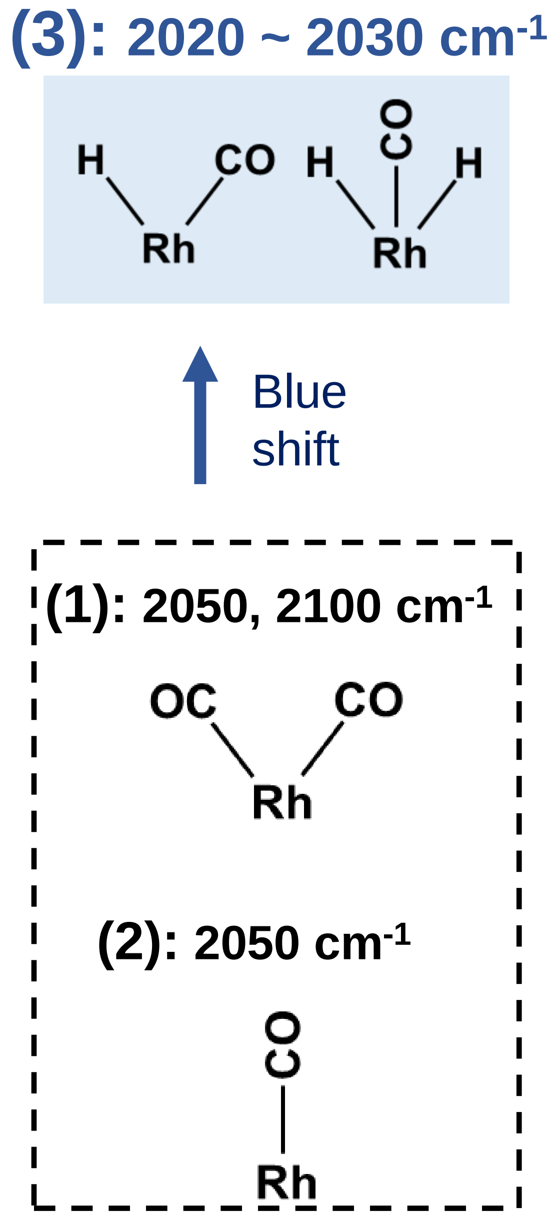
Rh-P : 2.388 Å

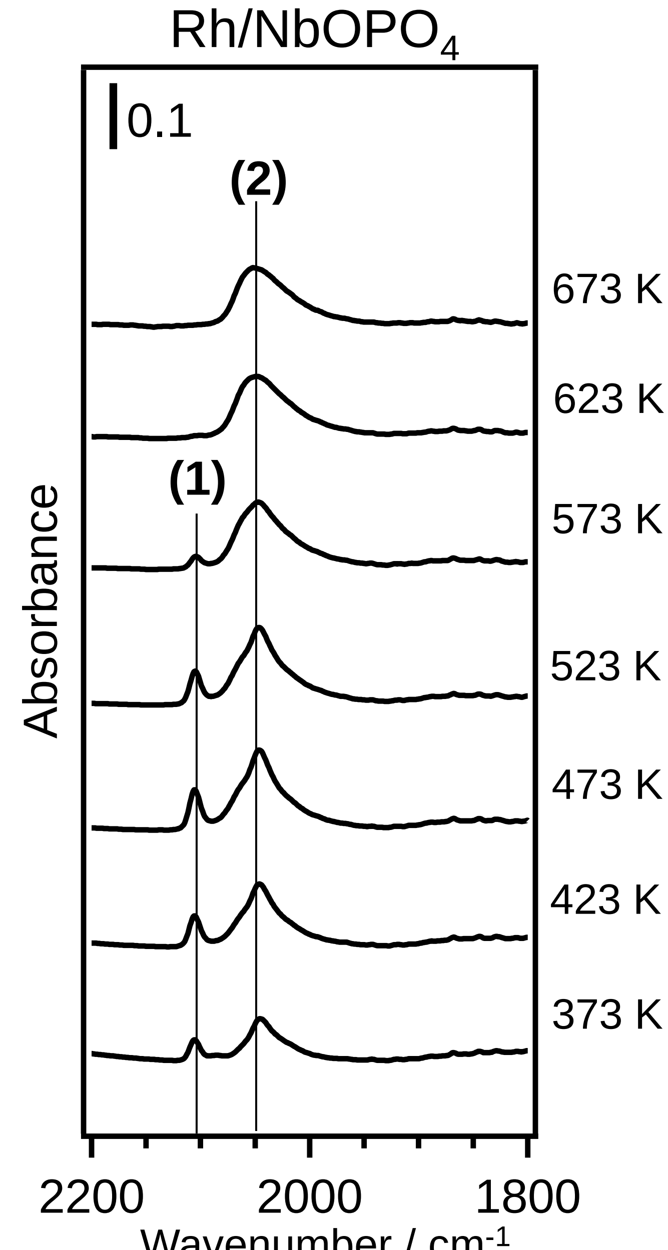
Rh-Rh : 2.758 Å

Rh-Rh : 2.701 Å

In situ DRIFT in CO_2/H_2 (1/4)

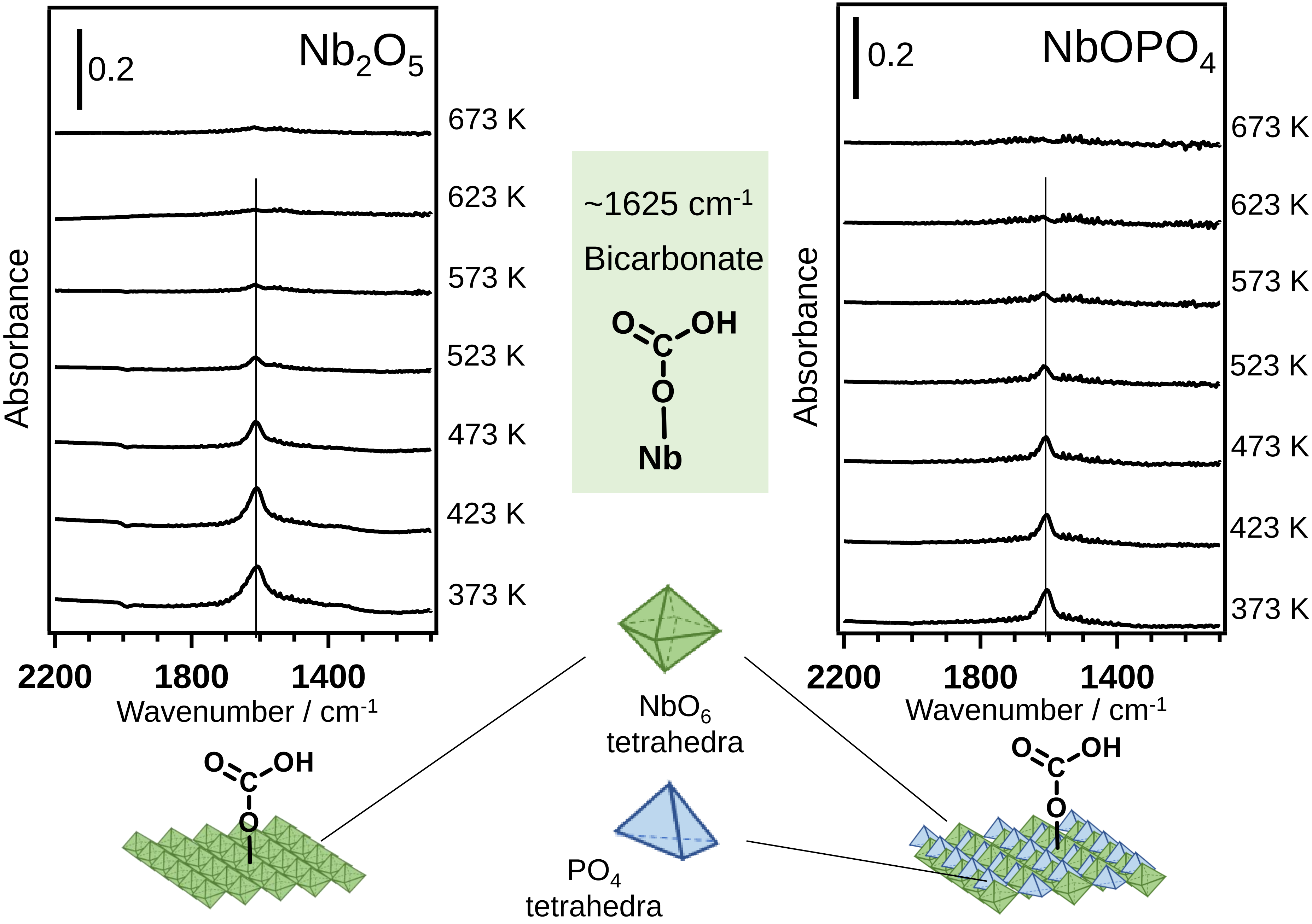






U. Bentrup et al., *ACS Catal.*, **2016**, *6*, 6275

In situ DRIFT in CO_2/H_2 (1/4)

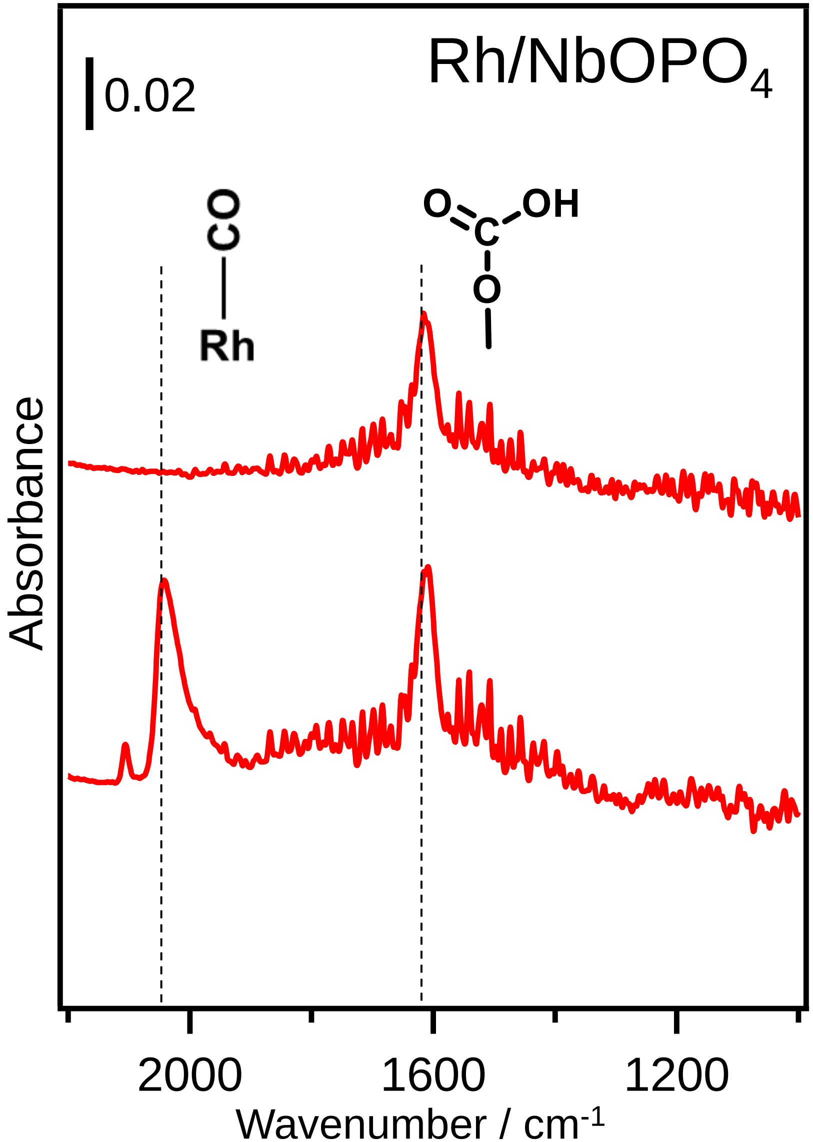


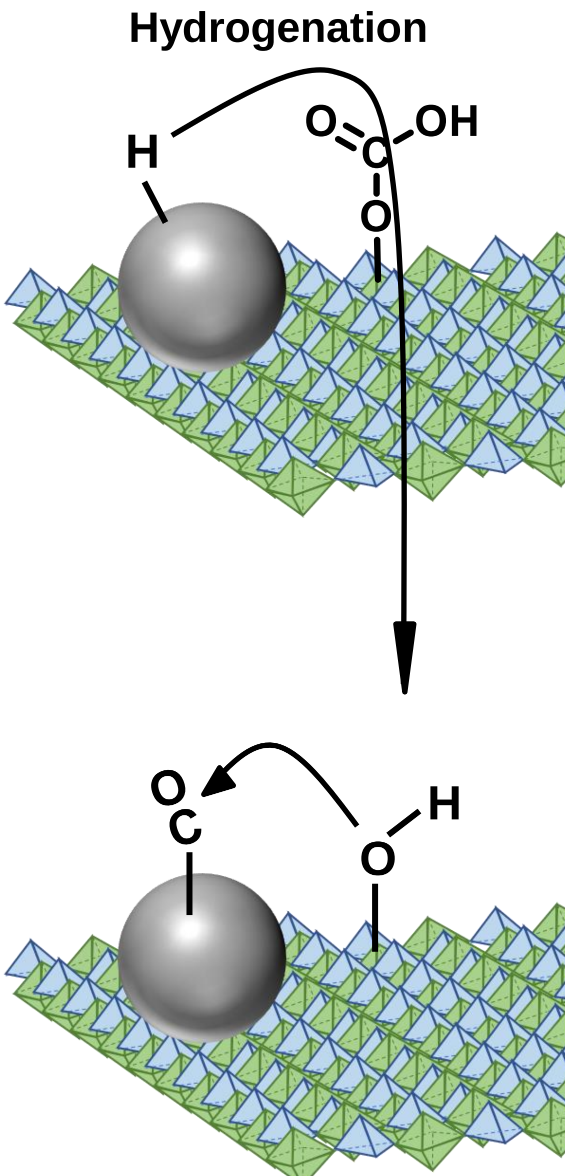
In situ DRIFT ($CO_2 \rightarrow H_2$)

Pretreatment:
H_2 reduction

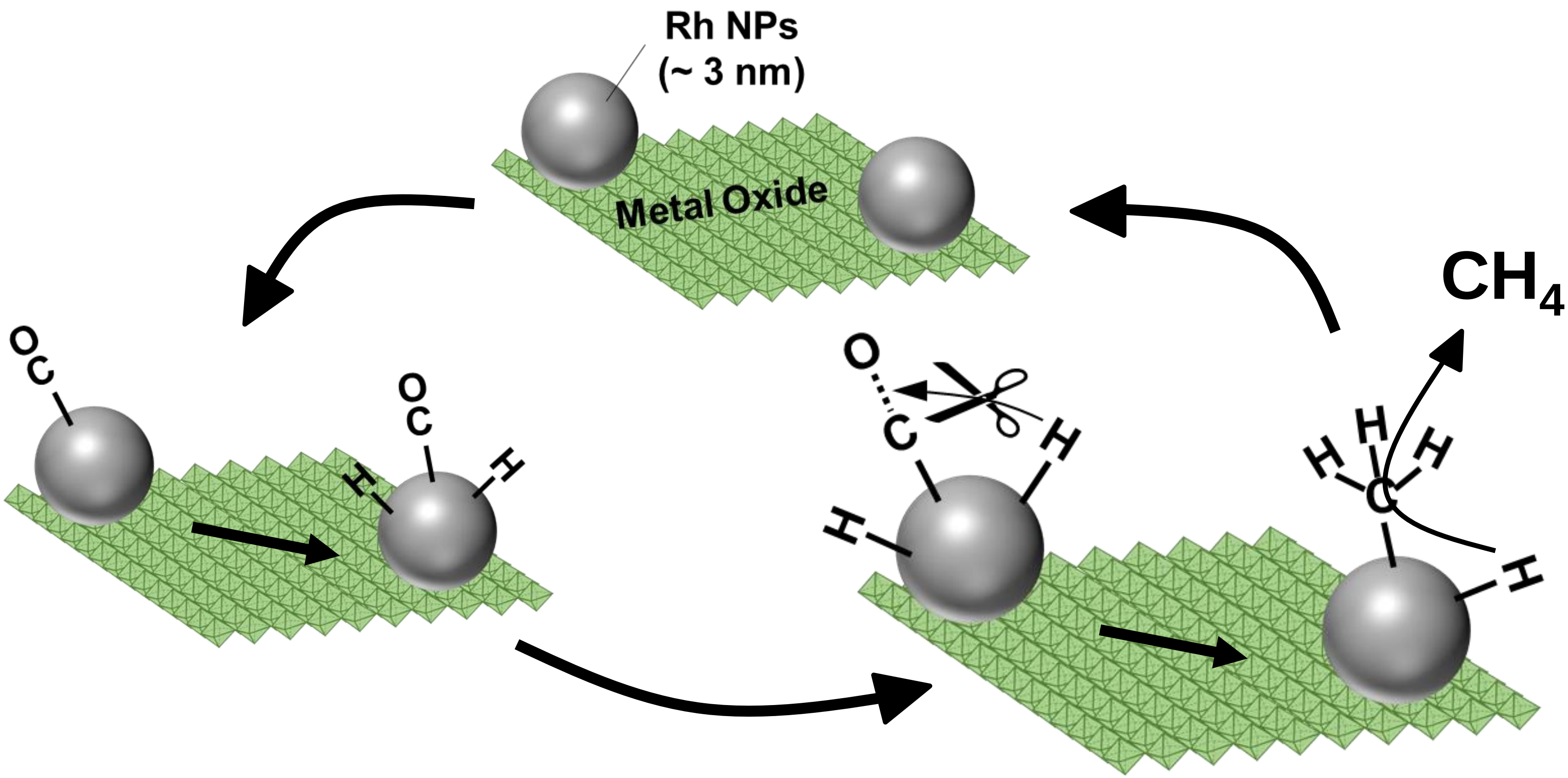
In CO_2 for 15 min at 523 K

After 1 min in H_2 at 523 K





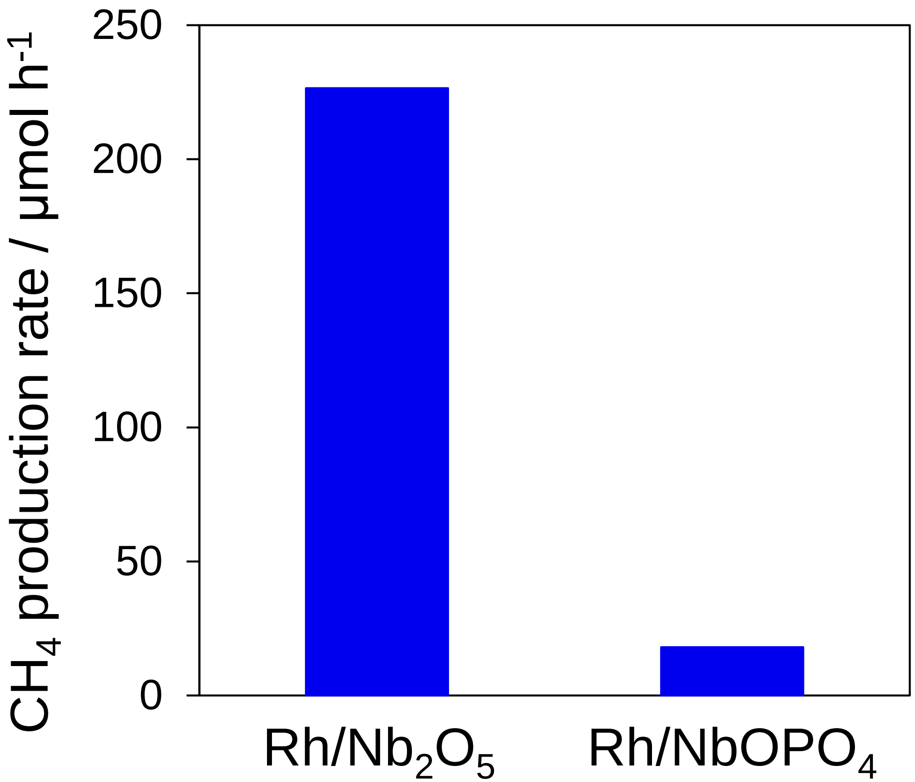
Mechanism of CO_2 methanation



▼ Methane was produced by sequential hydrogenation of CO.

CO hydrogenation

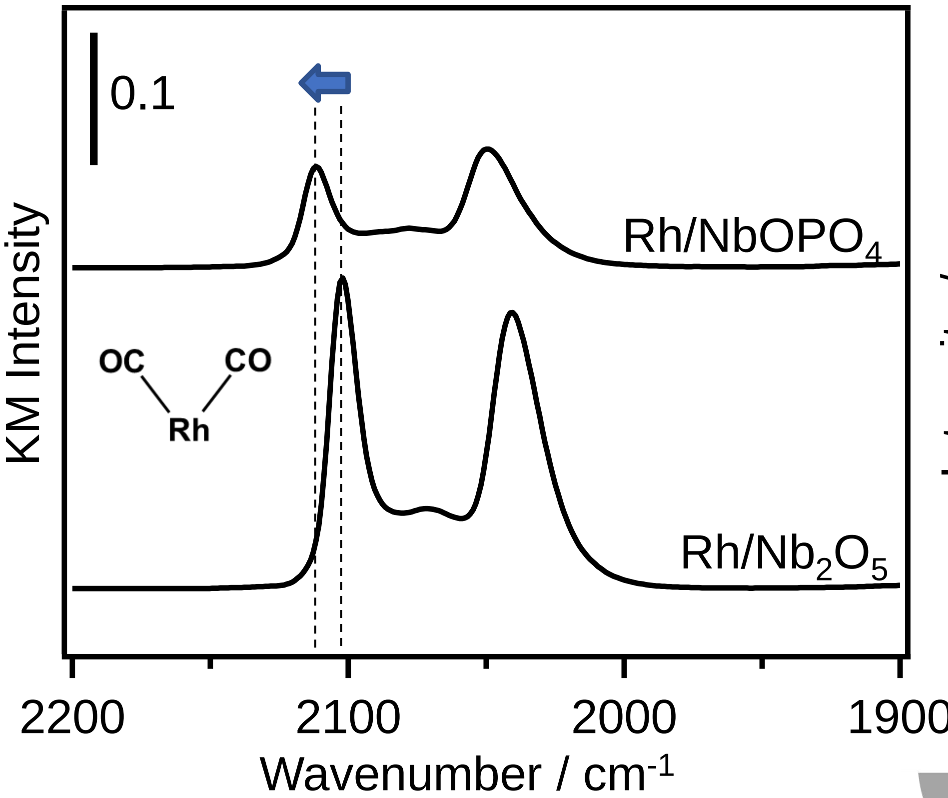
▼ CO hydrogenation scarcely proceeded on Rh/$NbOPO_4$.

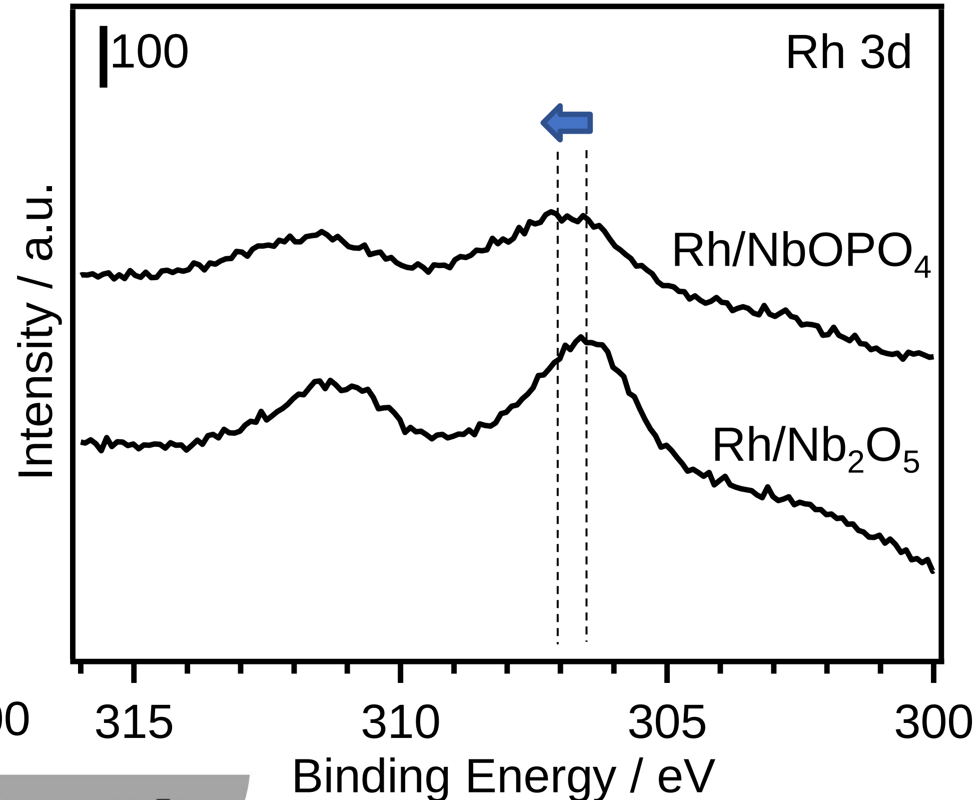


CH_4 production rate in CO hydrogenation
($CO + 3H_2 \rightarrow CH_4 + H_2O$) at 673 K

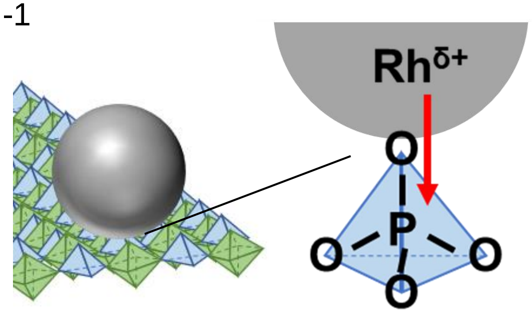
[CO Hydrogenation Condition] $CO/H_2/N_2/He$ = 10/40/5/45, GHSV = 60000 h^{-1} (Total: 100 mL min^{-1}, Catalysts: 100 mg), Pretreatment: H_2 reduction at 673 K for 1 h.

CO DRIFT and XPS





▼ Electron deficient Rh NPs were highly dispersed on phosphate.

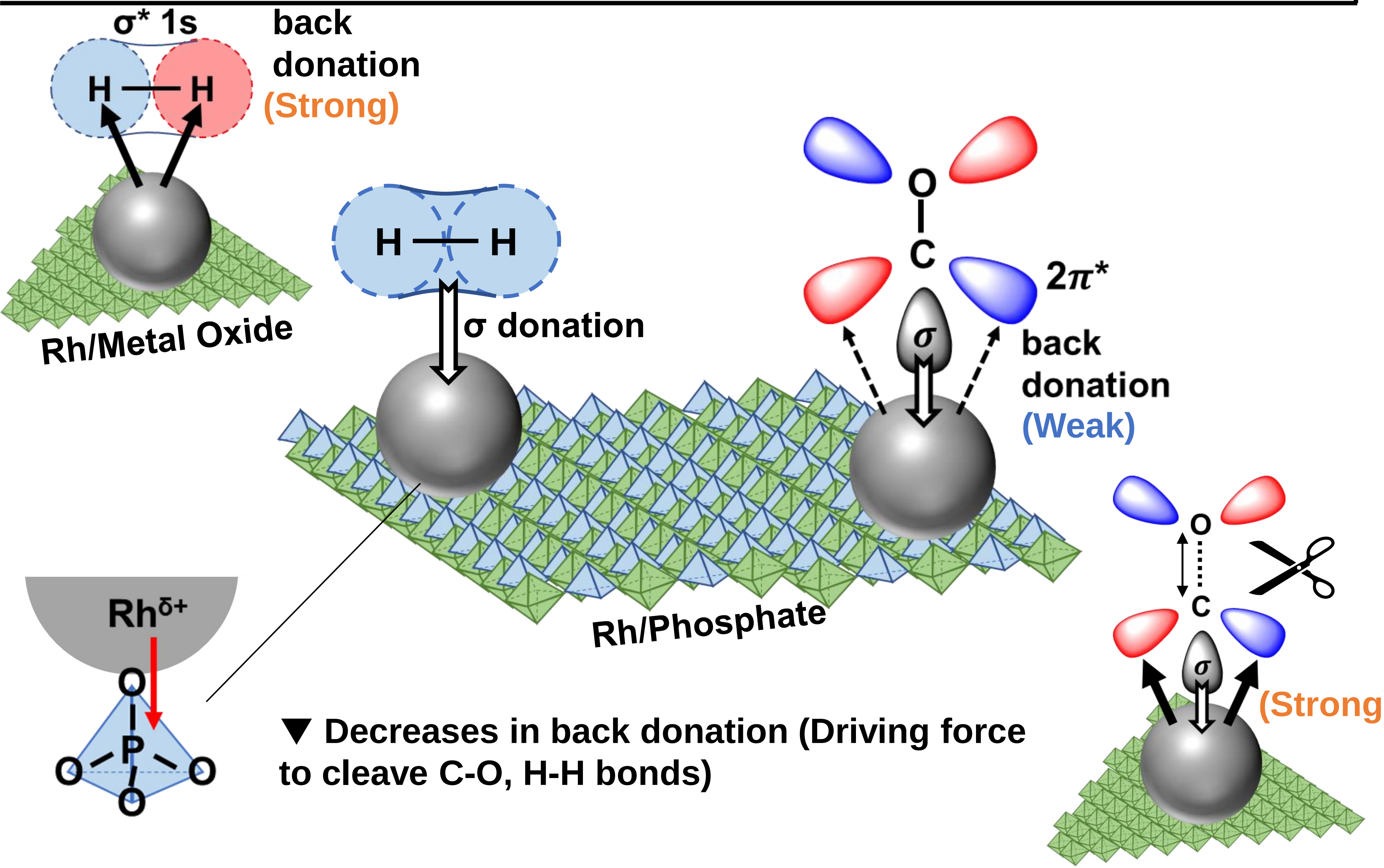


Electron-withdrawing effect of PO_4

[CO-DRIFT] H_2 reduction at 673 K for 1 h → CO adsorption for 10 min → He purge

[XPS] Pretreatment: H_2 reduction at 673 K for 1 h, Correction: C 1s (284.5 eV)
Samples were transported in the transfer vessel.

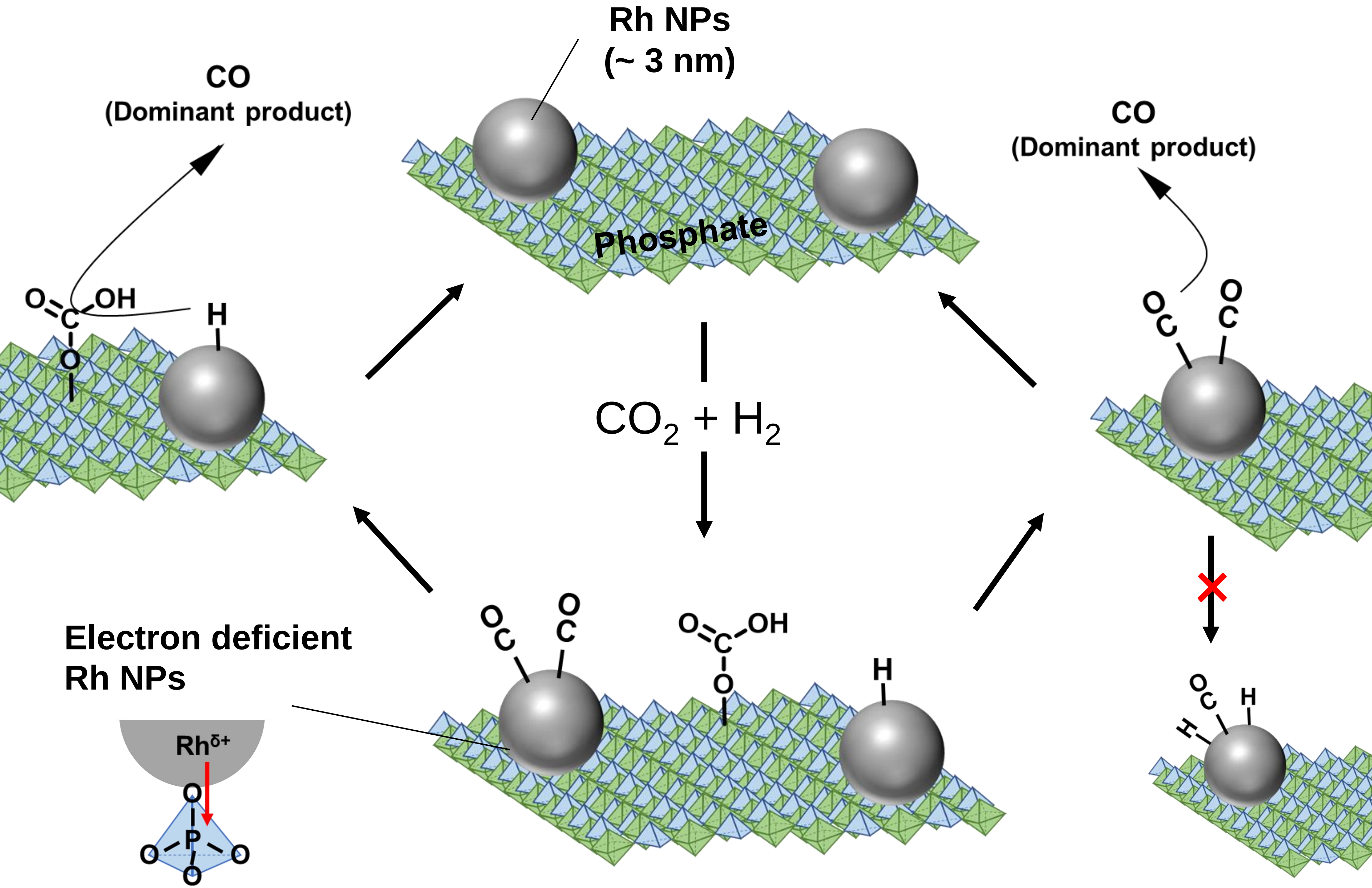
Electron deficient Rh



▼ Decreases in back donation (Driving force to cleave C-O, H-H bonds)

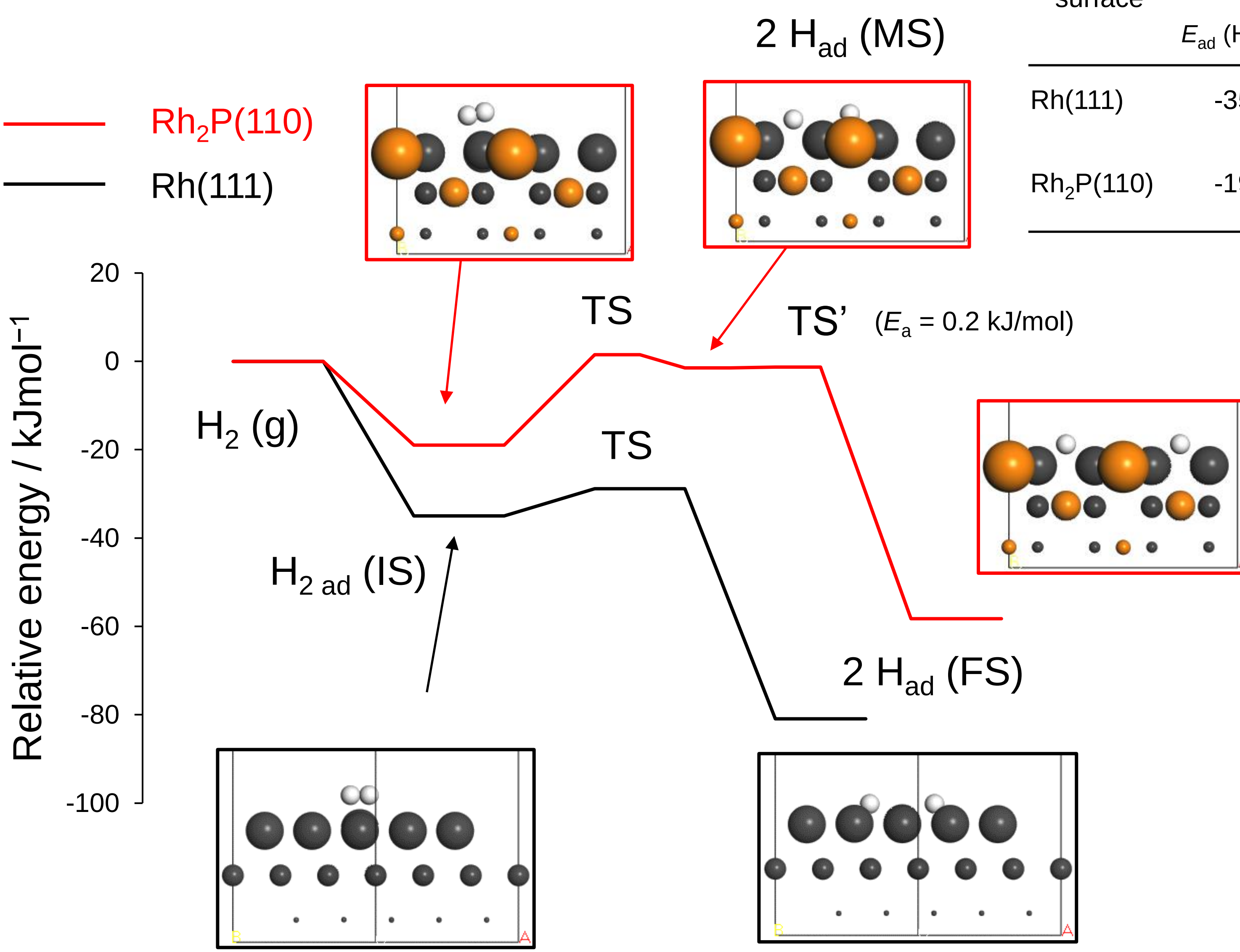
M. Machida et al., *ACS Catal.* **2015**, *5*, 1986 G. Broden et al., *Surf. Sci*. **1976**, *59*, 593

Electron deficient Rh

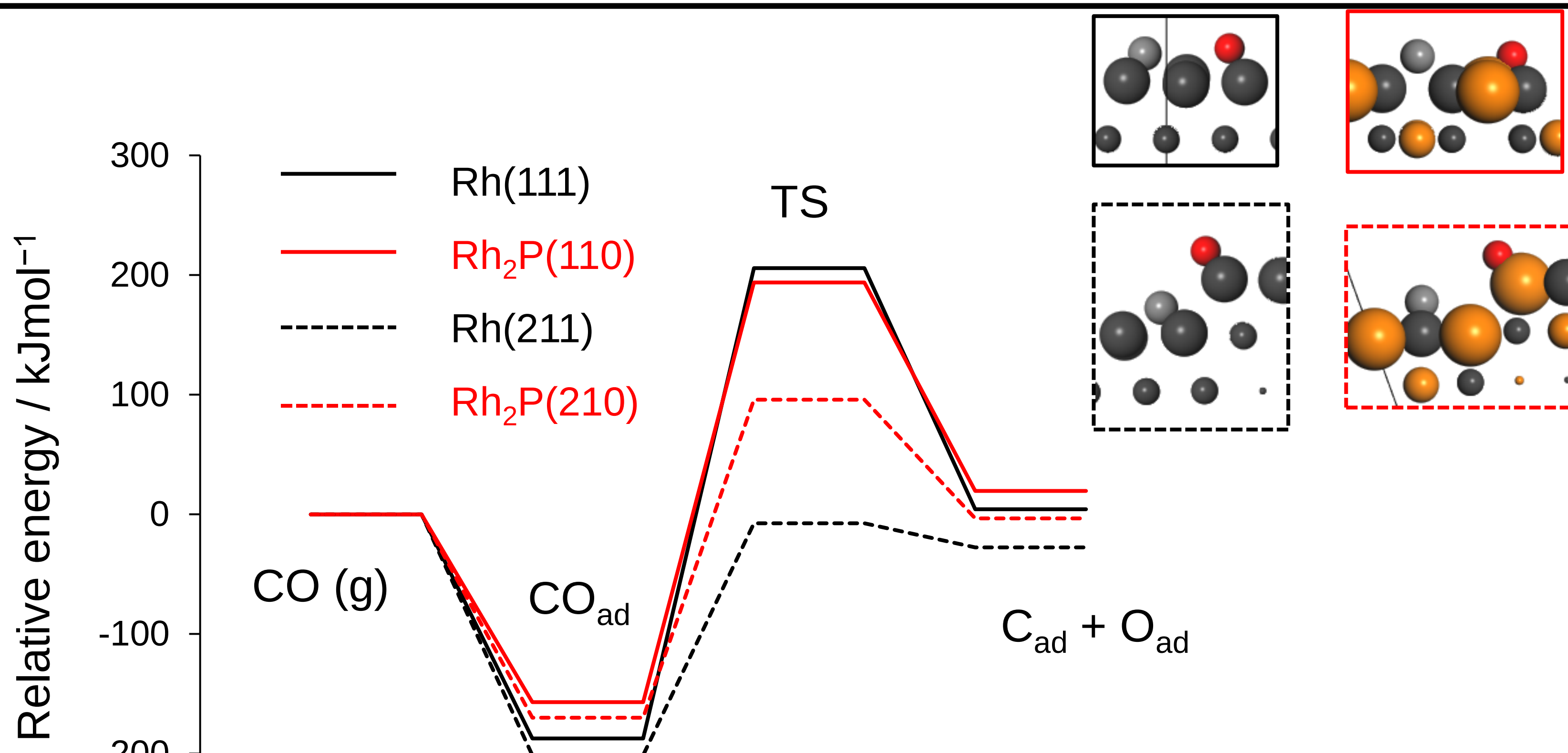


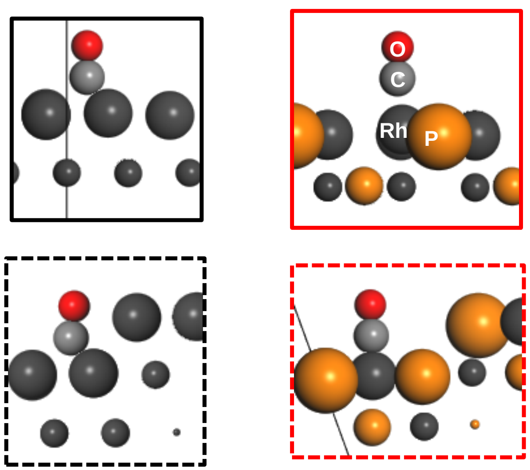
DFT: H_2 adsorption-dissociation

surface	Energy / kJmol⁻¹		
	E_{ad} (H_2)	E_a (H–H)	ΔE (H–H)
Rh(111)	-35.0	6.2	-45.9
$Rh_2P(110)$	-19.0	20.5	17.5 (-39.3)



DFT: CO adsorption-dissociation

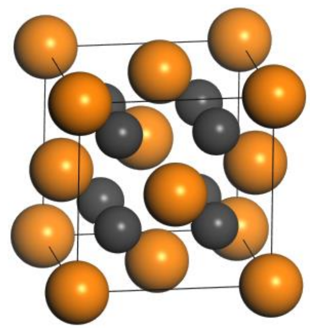




surface	Energy / kJmol^{-1}	
	E_{ad} (CO)	E_a
Rh(111)	-187.3	393.0
Rh_2P(110)	-157.1	351.0
Rh(211)	-201.5	194.0
Rh_2P(210)	-170.2	266.0

Summary

- Rh-P catalysts　CO selective
- Rh metal　CH_4 selective



Rh_2P

Rh_2P上では、COの（逐次的な）水素化が進行しない

水素の吸着・解離は速度論的にも熱力学的にもRhに比べ不利
COの脱離が促進、解離が抑制される

謝辞

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古川　森也　准教授

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