Towards Surface Chemistry of CO_2 from Synthetic Gases on Rh Catalyst

MS Colloquium

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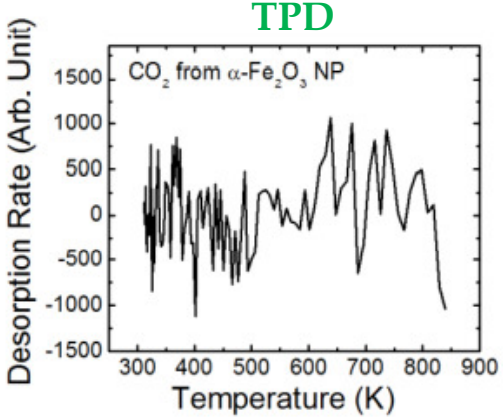
10/02/2023

Previous work from Our Group

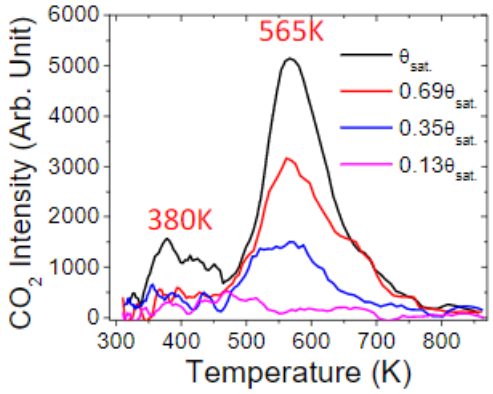
CO_2 surface chemistry- Temperature programmed desorption and Photodesorption

TPD



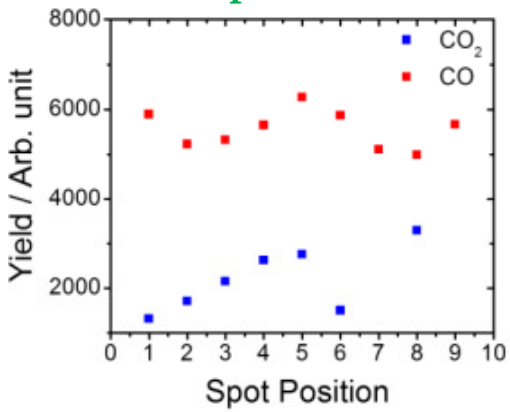
CO_2 adsorption is not active on TiO_2 supported Fe_2O_3 surface in room temperature

TPD



CO_2 adsorption is active on TiO_2 supported Pd- doped Fe_2O_3 surface in room temperature

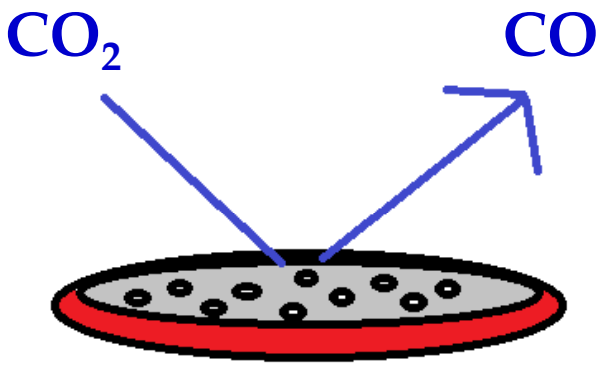
Photodesorption Measurement



CO_2 is also dissociating to CO

Bera, A., Banerjee, S., Bhattacharya, A., Tiwari, N., Jha, S. N., & Bhattacharyya, D. (2018). Morphology, Stability, Structure, and CO_2–Surface Chemistry of Micelle Nanolithographically Prepared Two-Dimensional Arrays of Core–Shell Fe–Pd Multicomponent Nanoparticles. *The Journal of Physical Chemistry C*, *122*(46), 26528-26542.

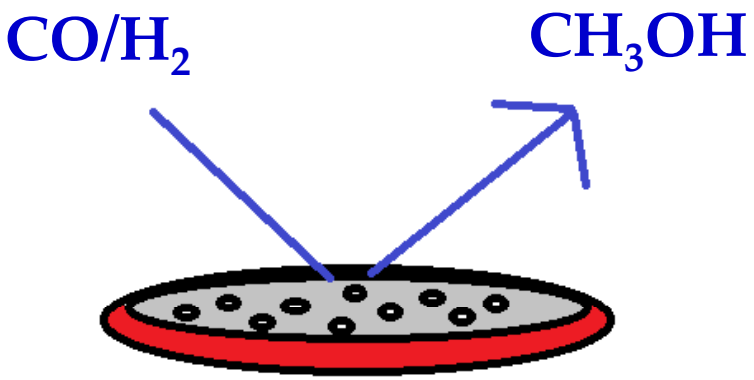
CO_2 adsorption and dissociation on metal surface



Rh is active catalyst for CO_2 adsorption and dissociation

Ref-Spivey, J.J. and Egbebi, A., 2007. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chemical Society Reviews*, *36*(9), pp.1514-1528.

Effective Catalyst of Methanol



Rh is active Catalyst for Methanol Synthesis from synthetic Gases

The process has not been industrialized yet for bulk synthesis

Ref-Spivey, J.J. and Egbebi, A., 2007. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chemical Society Reviews*, *36*(9), pp.1514-1528.

Why and How to Produce Methanol

Why?

1. Hydrogen Energy Carriers
2. Resource of different organic compounds
1. Alternative Fuel cells

How?

CO_2
CO
H_2
H_2O

Synthetic Gases

Catalytic Conversion →

Methanol

Problem-1

What is the Reaction Mechanism?

1st proposed Mechanism

$CO \longleftrightarrow CO^*$

$H_2 \longleftrightarrow 2H^*$

$CO^* \longleftrightarrow C^* + O^*$

$C^* + 3H^* \longleftrightarrow CH_3^*$

$CH_3^* + O^* \longleftrightarrow CH_3O^*$

$CH_3O^* + H^* \longleftrightarrow CH_3OH^*$

2nd proposed Mechanism

$CO \longleftrightarrow CO^*$

$H_2 \longleftrightarrow 2H^*$

$H^* + CO^* \longleftrightarrow HCO^*$

$HCO^* + 2H^* \longleftrightarrow CH_3O^*$

$CH_3O^* + H^* \longleftrightarrow CH_3OH^*$

What is the exact Pathway?

Ref-1.Spivey, J.J. and Egbebi, A., 2007. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chemical Society Reviews*, *36*(9), pp.1514-1528.

2. Choi, Y. and Liu, P., 2009. Mechanism of ethanol synthesis from syngas on Rh (111). *Journal of the American Chemical Society*, *131*(36), pp.13054-13061.

Problem-2

How can we achieve very good selectivity towards Methanol?

Side Reaction

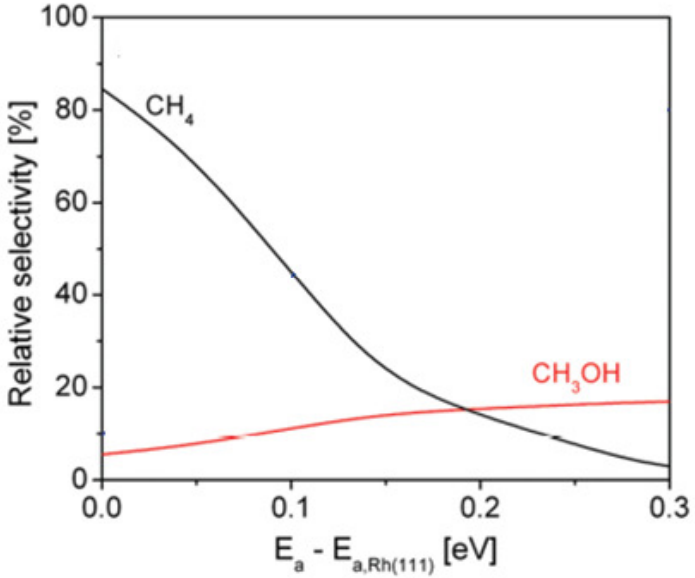
$$CH_3^* + H^* \longleftrightarrow CH_4^*$$

Due to this side reaction the selectivity is low towards Methanol

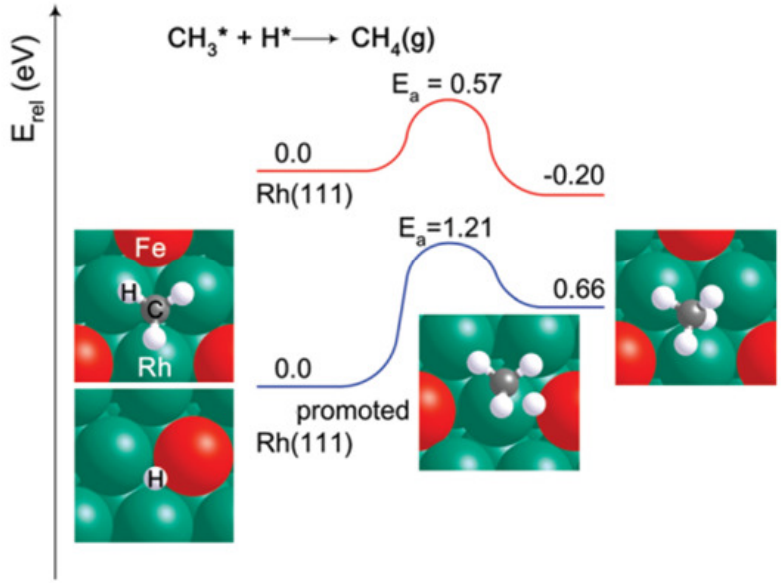
How can we increase selectivity towards Methanol?

Ref-1.Spivey, J.J. and Egbebi, A., 2007. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chemical Society Reviews*, *36*(9), pp.1514-1528.
2. Choi, Y. and Liu, P., 2009. Mechanism of ethanol synthesis from syngas on Rh (111). *Journal of the American Chemical Society*, *131*(36), pp.13054-13061.

Plan of increasing selectivity



Effect of changing the reaction barrier of $CH_3^* + H^* \longleftrightarrow CH_4(g)$ on Rh(111) surface



Doping helps to achieve good selectivity towards Methanol synthesis

Ref- Choi, Y. and Liu, P., 2009. Mechanism of ethanol synthesis from syngas on Rh (111). *Journal of the American Chemical Society*, *131*(36), pp.13054-13061.

Targets

$$CO_2 \rightarrow CO \rightarrow CH_3OH$$

1. CO_2 dissociation on Rh(111) catalyst and effect of 3d elements doping in this dissociation

2. Understanding the reaction mechanism of Methanol synthesis

3. How to increase the selectivity of Methanol synthesis

CO_2 dissociation on Rh(111) catalyst and effect of 3d elements doping in this dissociation

The work has been performed with the help of periodic DFT calculation

CO_2 adsorption On Rh(111) surface

Linear CO_2 + Rh(111) surface ⟷ Bent CO_2 adsorbed on Rh(111) surface

Why?

Charge transfer occurs from Rh surface to CO_2

Ref-Kim, J., Ha, H., Doh, W.H., Ueda, K., Mase, K., Kondoh, H., Mun, B.S., Kim, H.Y. and Park, J.Y., 2020. How Rh surface breaks CO2 molecules under ambient pressure. *Nature communications*, *11*(1), pp.1-9.

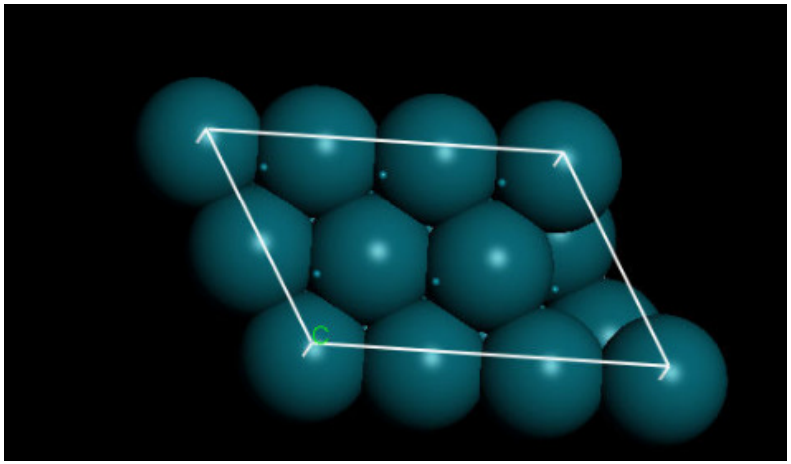
what are we exploring?

Dissociation Pathway

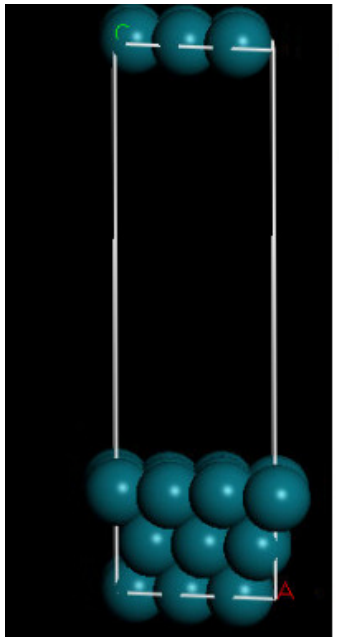
1. Bent CO_2 adsorbed on Rh(111) → Dissociated CO and O on Rh(111) surface

2. Effect of 3d element doping on Rh(111) in dissociation Pathway

Our computational model for Rh(111) surface



Top view of our constructed Rh(111) model surface



Font view of our constructed Rh(111) model surface

CASTEP in Material Studio 6.0.

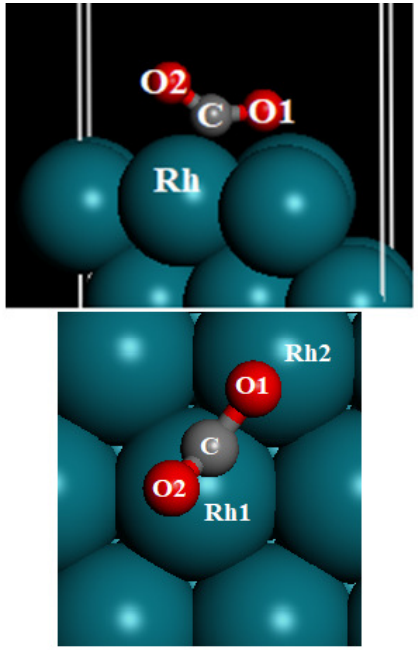
1. GGA – PBE functional
2. 3×4×1 k point set used
3. 20 Å Vacuum Slab
4. 3 layers
5. Energy Cut off = 300 eV

TS search- LST and QST method

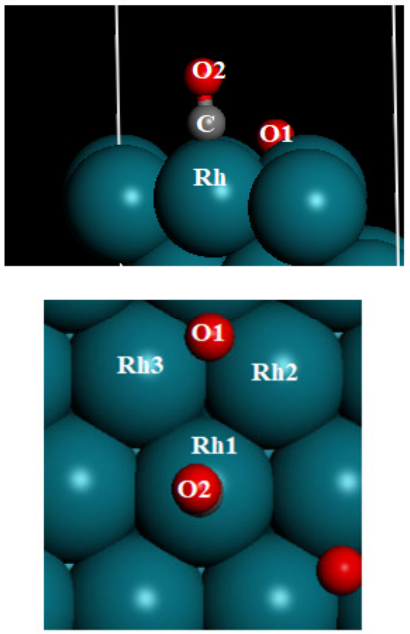
Structures of dissociation reaction

Font view

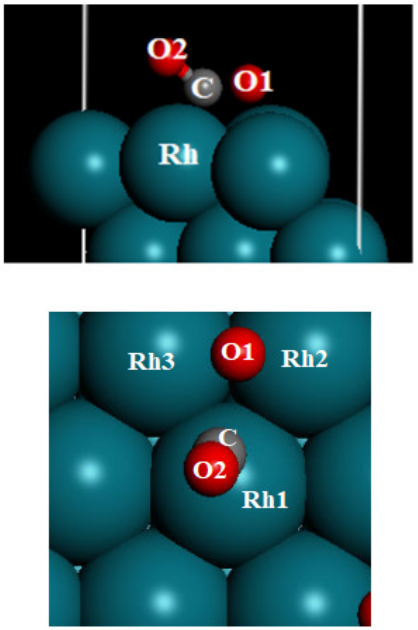
Top View



Bent adsorbed CO_2 on Rh(111) surface



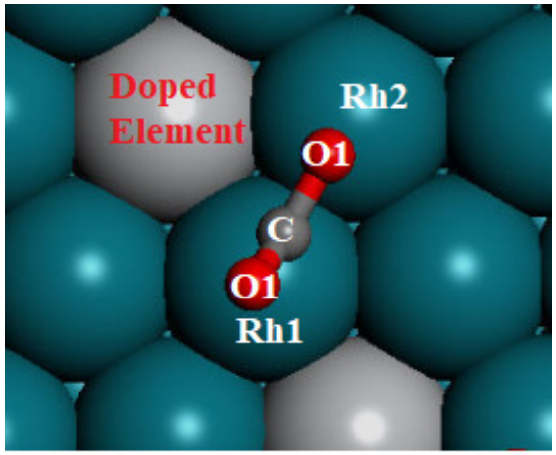
Dissociated CO on Rh(111) surface



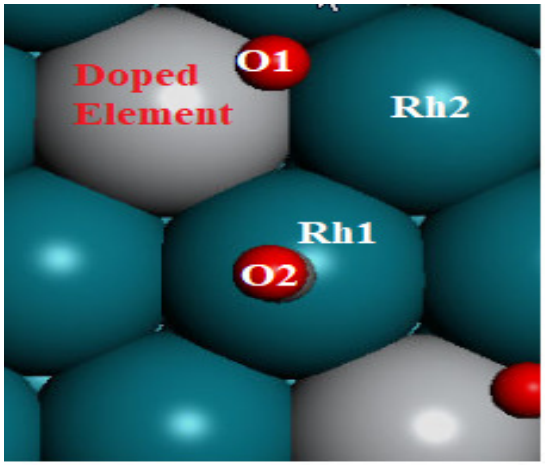
Transition state of dissociation on Rh(111) surface

Coverage = 0.33 (ML)

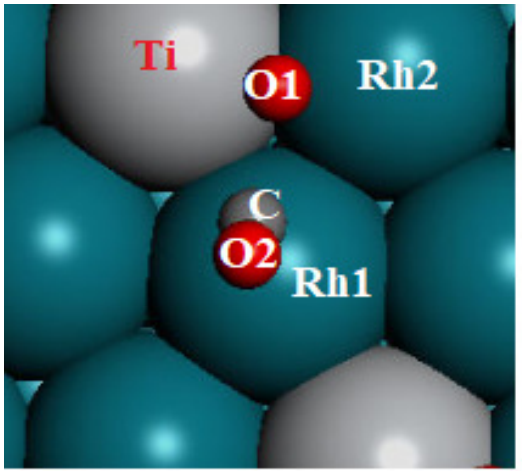
Structure for dissociation reaction on 3d element doped Rh(111) surface



Bent adsorbed CO_2 on 3d element doped Rh(111) surface



Dissociated CO on 3d element doped Rh(111) surface

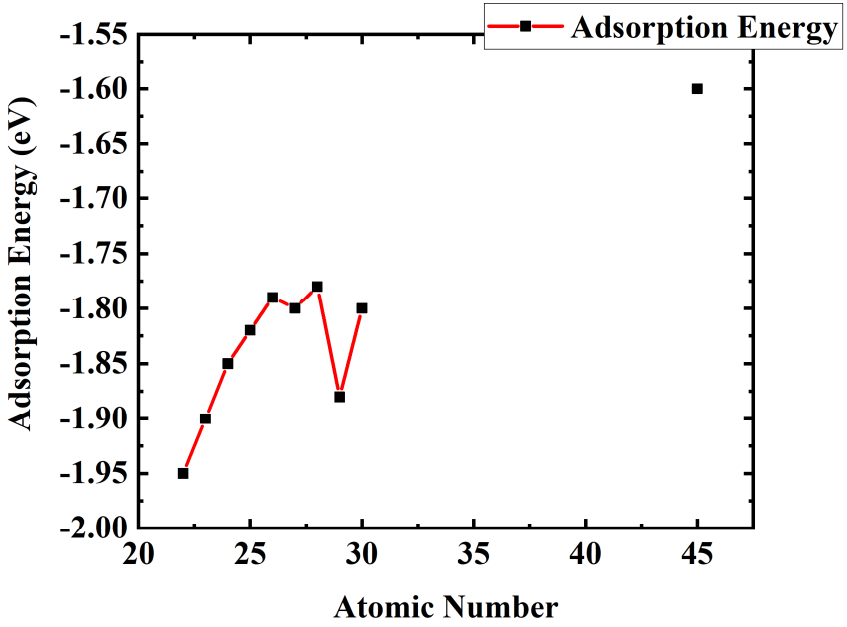


Transition state of dissociation on 3d element doped Rh(111) surface

1. We have doped Rh(111) surface using 3d elements from Ti to Zn.

2. Doping fraction $= \frac{1}{6}$

Results from Adsorbed surfaces



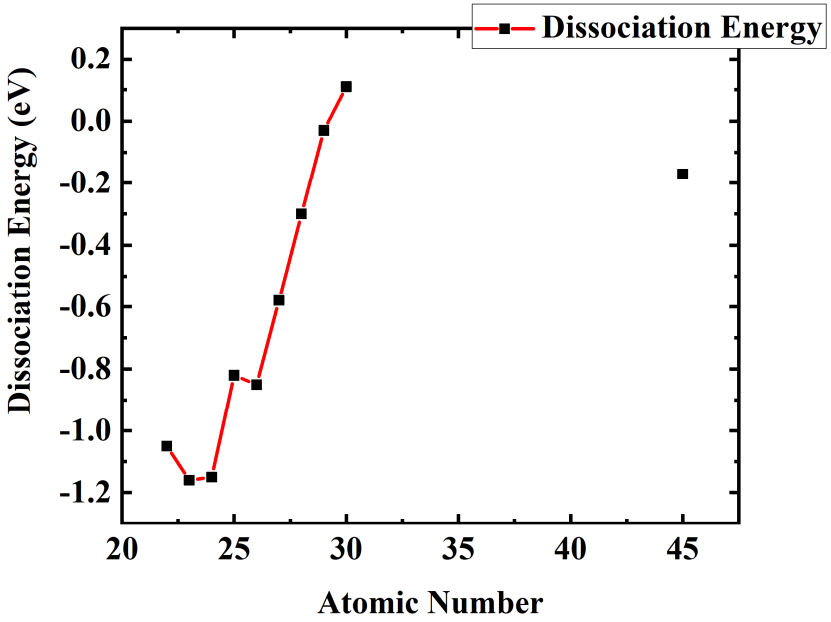
Adsorption Energy of CO_2 on doped Rh surface shows how the adsorption energy is changing with doping.

Conclusions-

Doping has positive effect of CO_2 adsorption

CO_2 can be adsorbed very easily on doped surface.

Results from dissociated CO

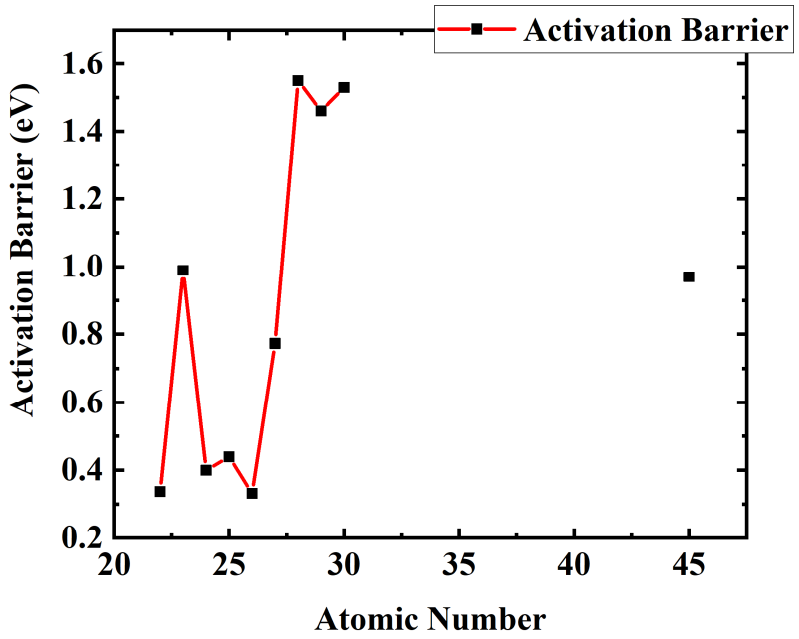


Dissociation Energy is higher (except Zn and Cu) than that of without doped elements

Conclusion-

Exothermicity increases except Cu and Zn with metal doping

Catalytic Activity of doped surface



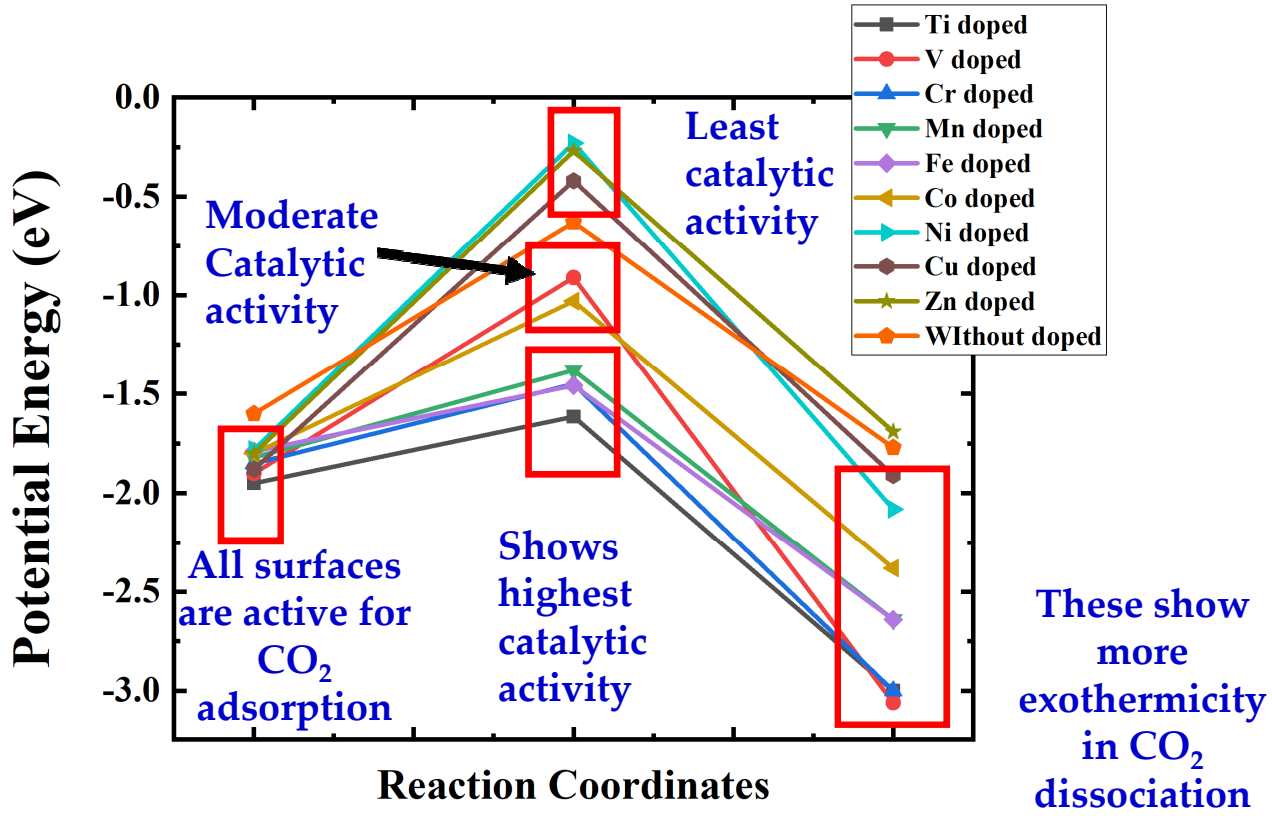
Conclusion-

Most of the doped surfaces show better catalytic activity than that of Rh(111) surface

Especially Ti, Cr, Mn and Fe are showing very good catalytic activity.

Ti , Mn, Cr and Fe are showing best doped elements among Ti to Zn.

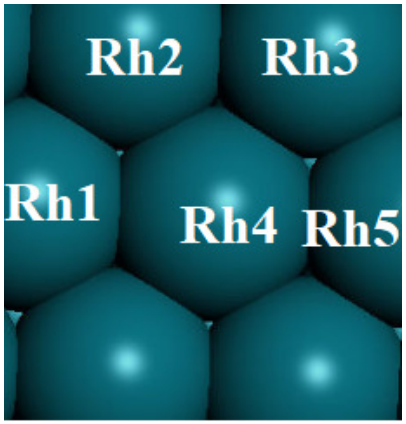
Conclusion of CO_2 dissociation



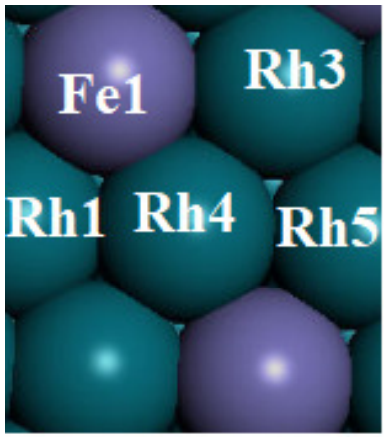
Understanding the reaction mechanism of Methanol synthesis on Rh(111) surface and effect of doping on selectivity

The work has been performed with the help of periodic DFT calculation

Structures

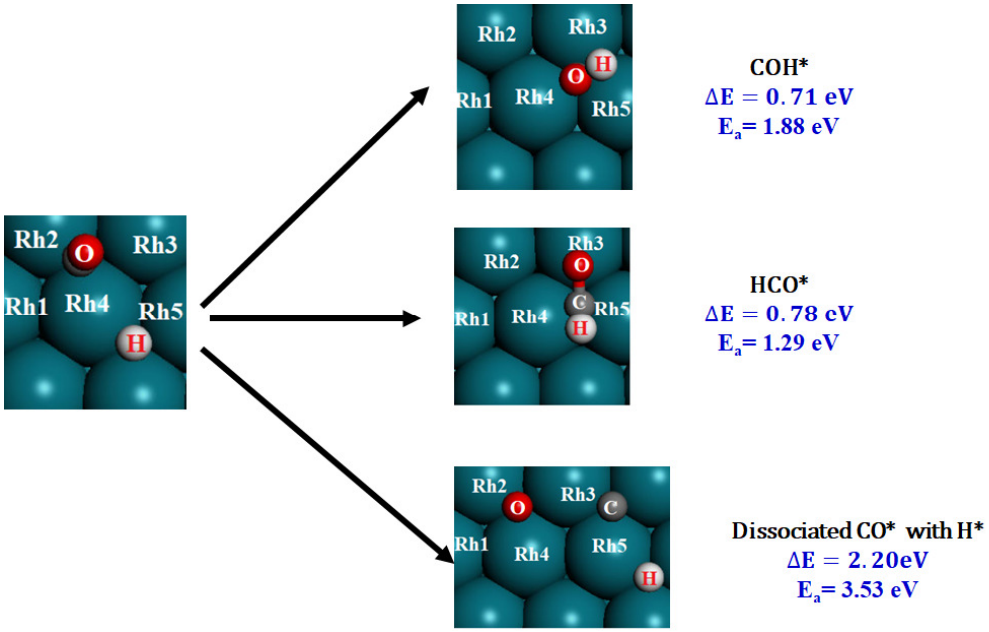


Without doped structure



Doped Structure

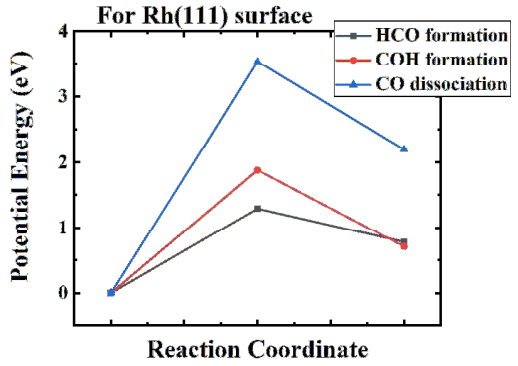
CO dissociation or HCO formation

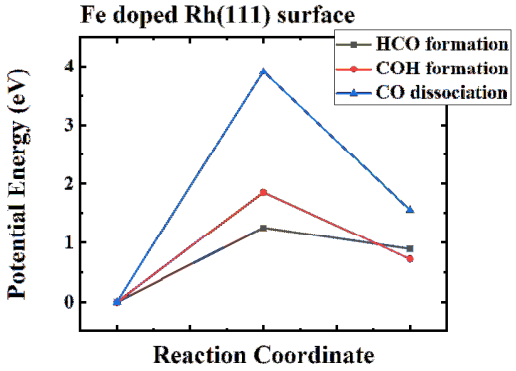


COH*
$\Delta E = 0.71$ eV
$E_a = 1.88$ eV

HCO*
$\Delta E = 0.78$ eV
$E_a = 1.29$ eV

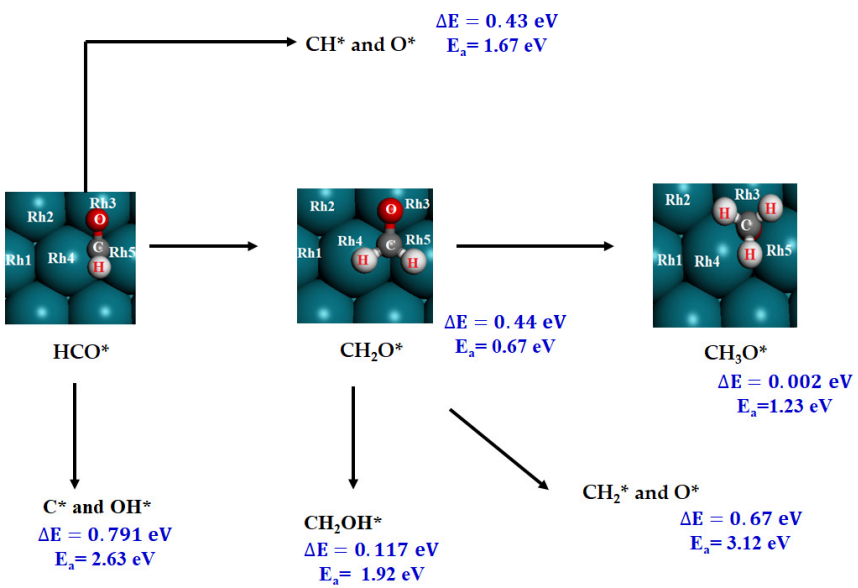
Dissociated CO* with H*
$\Delta E = 2.20$eV
$E_a = 3.53$ eV

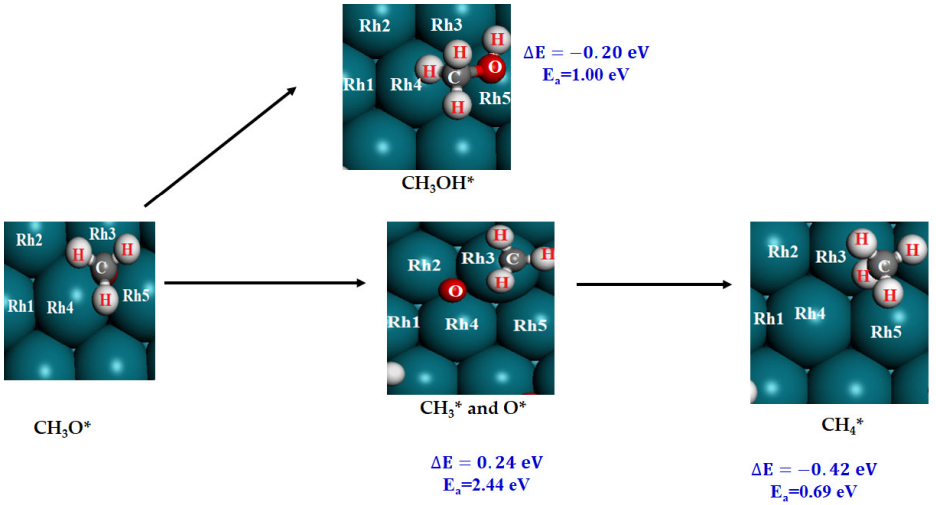




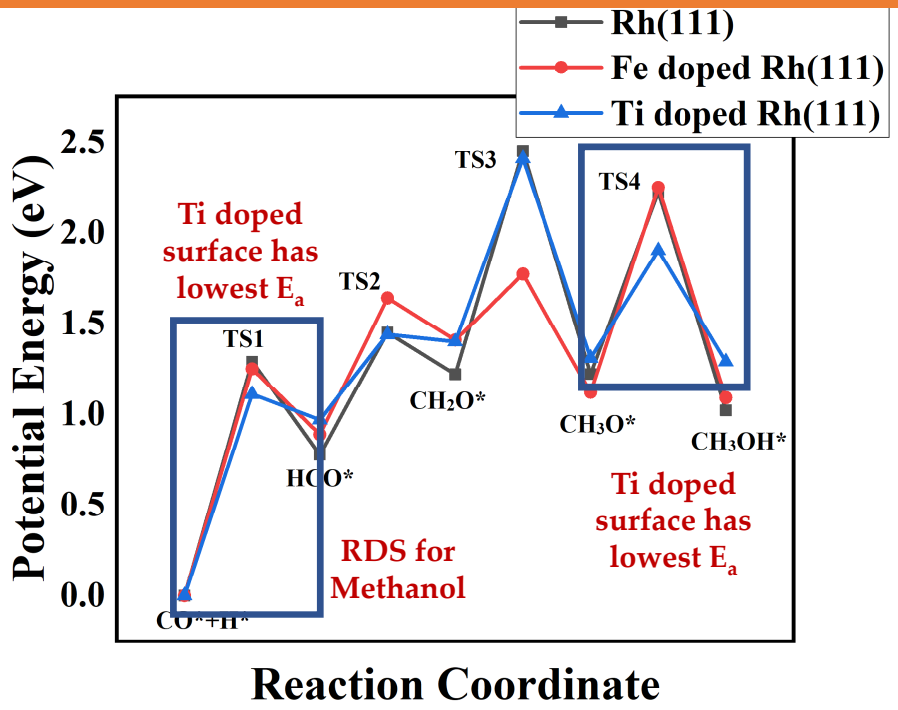
HCO formation is favorable not CO dissociation

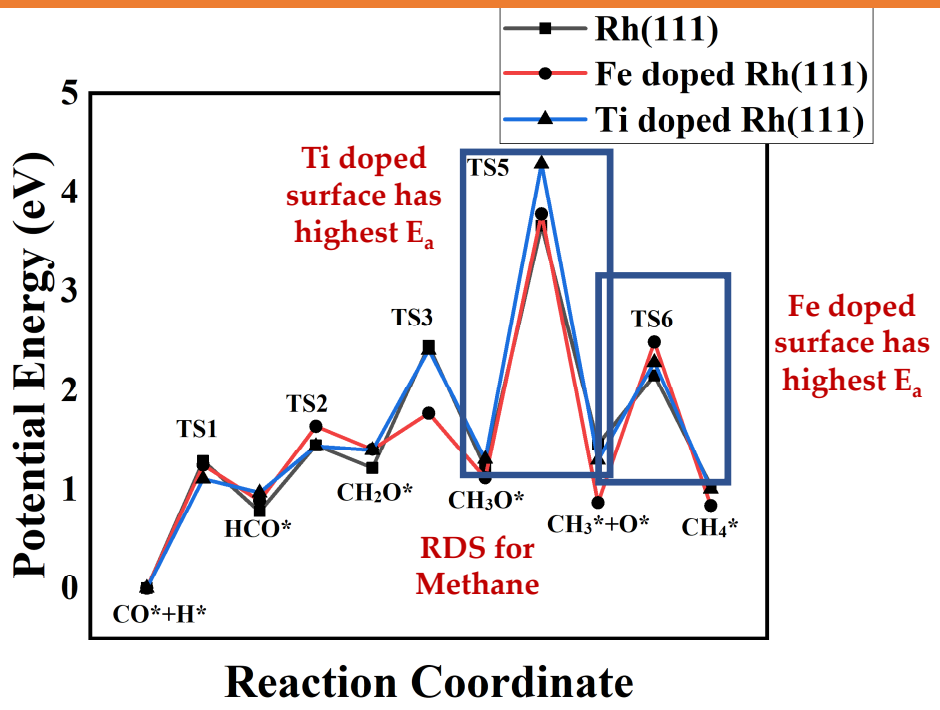
Predicting Reaction Mechanism on Rh(111) surface





Conclusion





Methanol selectivity-
Ti doped Rh(111) surface is the best

Conclusion

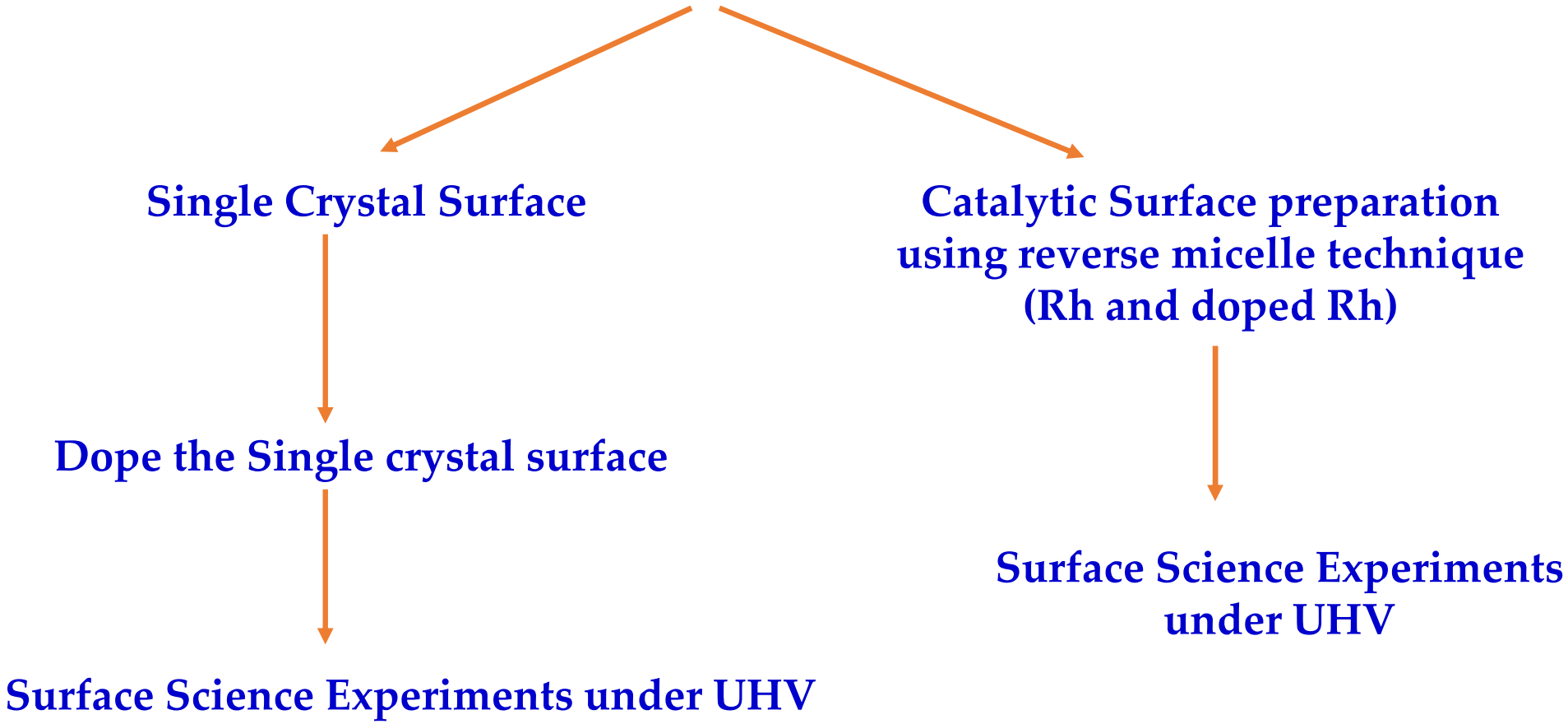
1.Computational Model shows HCO formation is more kinetically favorable than that of C-O dissociation.

2. Mechanism of Methanol formation is $CO \rightarrow HCO \rightarrow CH_2O \rightarrow CH_3O \rightarrow CH_3OH$

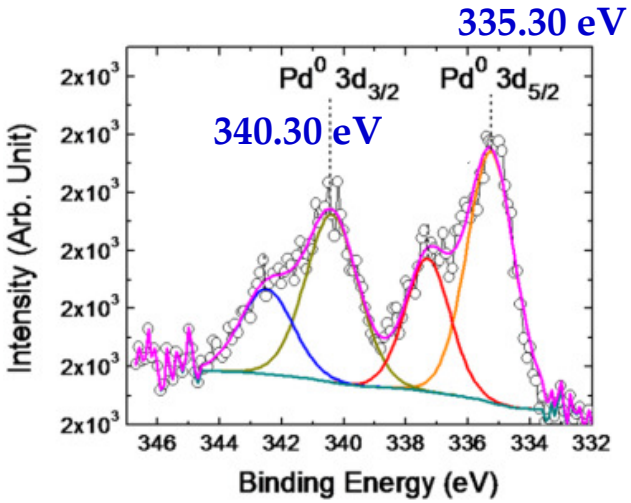
3. Ti doped Rh(111) surface shows best selectivity for CH_3OH formation.

Experimental Efforts

Surface science experiments



Previous works from Chemical Dynamics Lab



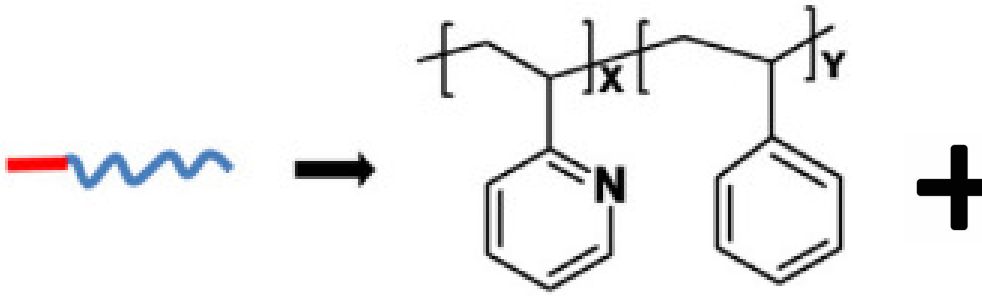
XPS spectra of Pd^0 after high temperature annealing at 600^0C of Fe-Pd bimetallic surface

We are expecting to get similar result from Rh surface also.

Ref-Bera, A., Banerjee, S., Bhattacharya, A., Tiwari, N., Jha, S.N. and Bhattacharyya, D., 2018. Morphology, Stability, Structure, and CO_2–Surface Chemistry of Micelle Nanolithographically Prepared Two-Dimensional Arrays of Core–Shell Fe–Pd Multicomponent Nanoparticles. *The Journal of Physical Chemistry C*, *122*(46), pp.26528-26542.

Model Catalytic Surface Preparation

Reverse Micelle Technique



+ **Toluene**

Inside the Glove Box →

Solution 1

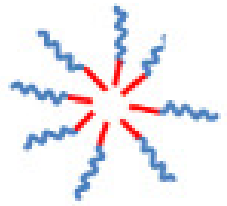
50 mg polymer

Polystyrene- block-poly(2- vinylpyridine)

Used as Copolymer
Red- Hydrophilic part
Blue- Hydrophobic part

10 mL

Non polar solvent



Reverse Micelle

Ref-Bera, A., Banerjee, S., Bhattacharya, A., Tiwari, N., Jha, S.N. and Bhattacharyya, D., 2018. Morphology, Stability, Structure, and CO_2–Surface Chemistry of Micelle Nanolithographically Prepared Two-Dimensional Arrays of Core–Shell Fe–Pd Multicomponent Nanoparticles. *The Journal of Physical Chemistry C*, *122*(46), pp.26528-26542.

Model Catalytic Surface Preparation

Solution 1 + Rhodium acetyl acetate

0.25 (M)

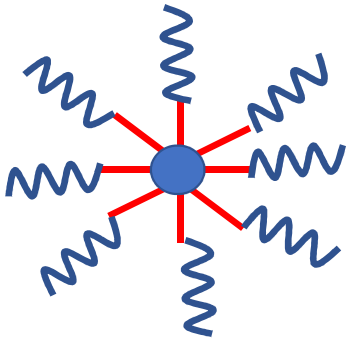
Inside the Glove Box →

Solution was stirred for 80^0c for 12 hour

↓ Inside the Glove Box

Stirred at room temperature for 2 days

← Inside the Glove Box

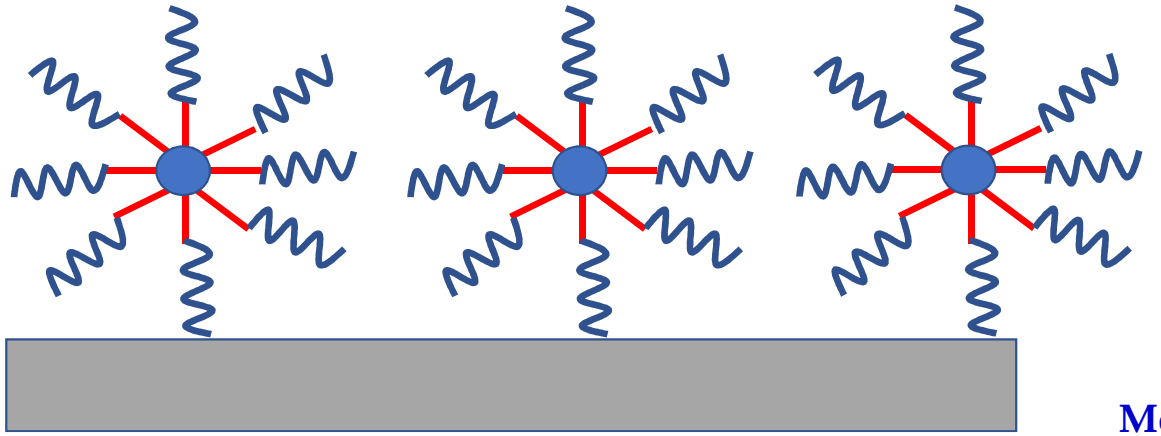


Loaded Reverse Micelle

Model Catalytic Surface Preparation

Loaded Reverse Micelle + **Silicon Wafer**

Spin Coating at 4400 rpm for 1 min



Pseudohexagonal array of metal

Model Catalytic Surface on support surface

Final Conclusion

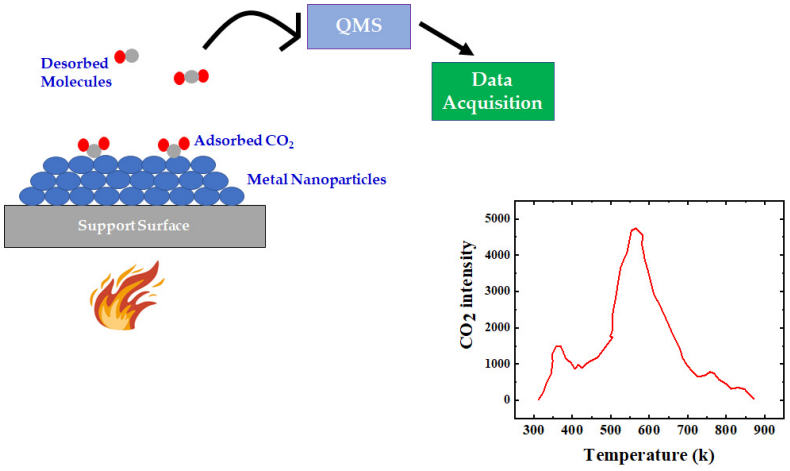
1. We have explored CO_2 dissociation pathway on Rh(111) catalyst and 3d element doped Rh(111) catalyst by computational methos and observed Fe and Ti doping on Rh(111) surface are very good robust system for CO_2 dissociation.

2. We also explored methanol preparation mechanism on Rh(111) surface and Ti and Fe doped Rh(111) system. Ti and Fe doping on Rh(111) system may increase selectivity towards methanol.

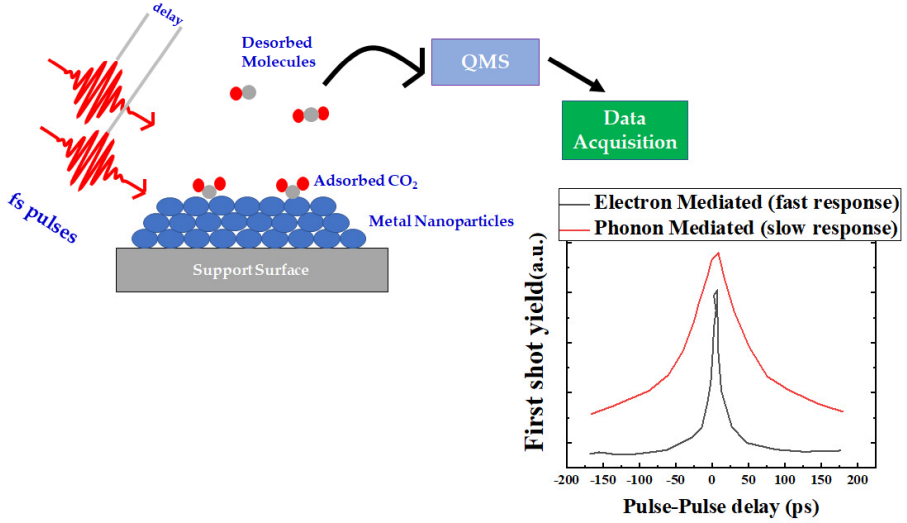
3. We have prepared Rh nano-catalytic surface with reverse micelle nanolithography.

Future Outlook

1. **Surface Science study using Temperature Programmed Desorption Reaction**



2. **Photo-desorption using 2 Pulse Correlation Spectroscopy**



THANK YOU

Acknowledgement

Dr. Atanu Bhattacharya (Advisor)

Arpan Chakraborty (Experiments and Discussion)

Dr. Sampad Bag, Binoy Paine, Apurba Manna (Labmates)

CeNSE, IISc (SEM)

SERC (CASTEP calculation)

Dr. Sourav Banerjee (CASTEP calculation)

Anik, Sourav, Sudip Da, Indranil Da, Susen, Apurba, Rounab, Soham Da, Ritwika di, Aishita di, Simpa

My Parents

Financial Support -DST Nano Mission, Institute fellowship

THANKS FOR YOUR KIND ATTENTION

BACK UP SLIDES

Reaction data and effect of doping

Reactions	Activation Energy for Rh(111) surface (eV)	Activation Energy for Fe doped Rh(111) surface (eV)	Activation Energy for Ti doped Rh(111) surface (eV)
$CO^* + H^* \rightarrow HCO^*$	1.29	1.25	1.11
$HCO^* + H^* \rightarrow CH_2O^*$	0.67	0.75	0.47
$CH_2O^* + H^* \rightarrow CH_3O^*$	1.23	0.36	1.01
$CH_3O^* \rightarrow CH_3^* + O^*$	2.44	2.58	2.98
$CH_3^* + H^* \rightarrow CH_4^*$	0.69	1.62	0.986
$CH_3O^* + H^* \rightarrow CH_3OH^*$	1.00	1.13	0.597
$CO^* + H^* \rightarrow COH^*$	1.87	1.85	-
$CO^* + H^* \rightarrow C^* + O^* + H^*$	3.53	3.91	-

Lowest for Ti doped surface

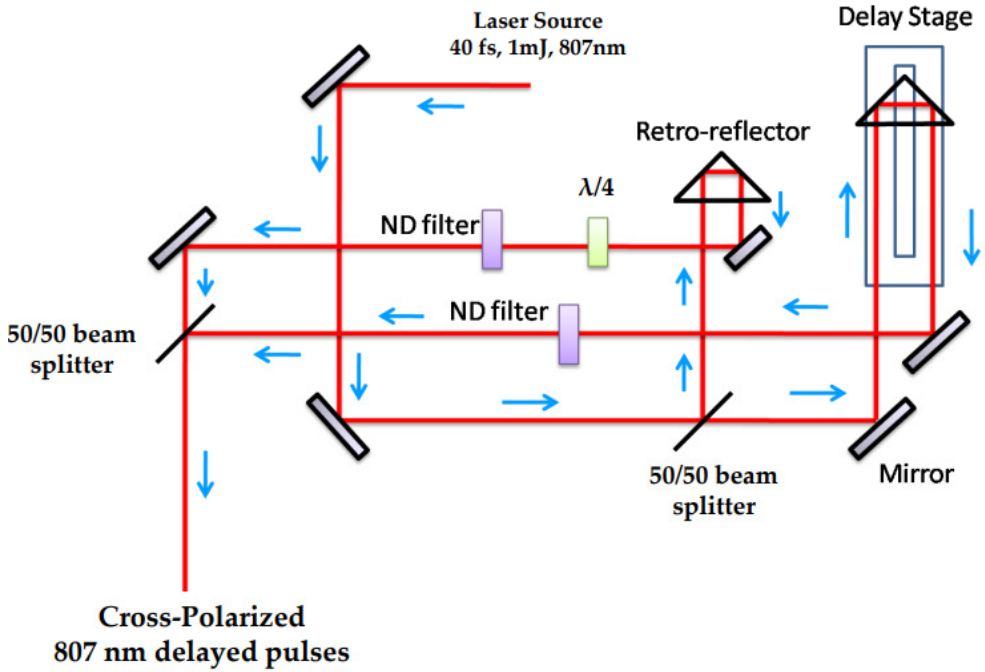
Highest for Ti doped Surface

Highest for Fe doped Surface

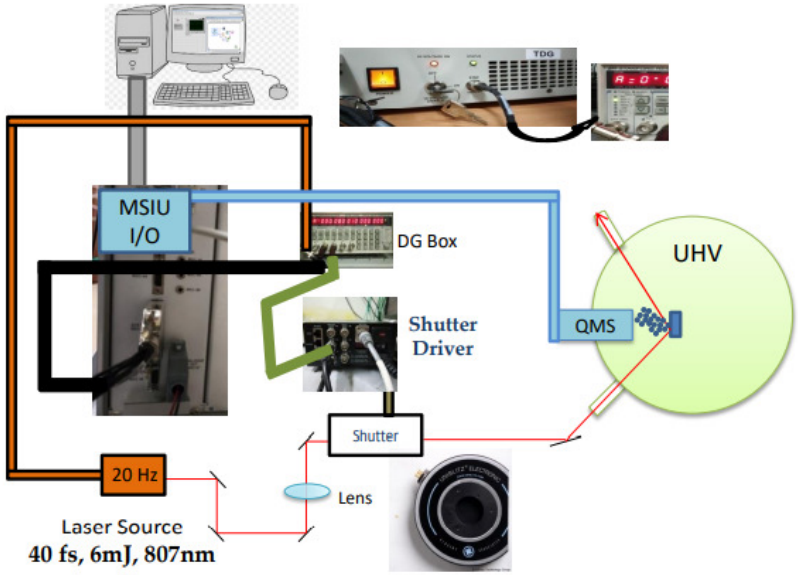
Lowest for Ti doped Surface

2 Pulse Correlation Spectroscopy

Time Resolved Spectroscopy



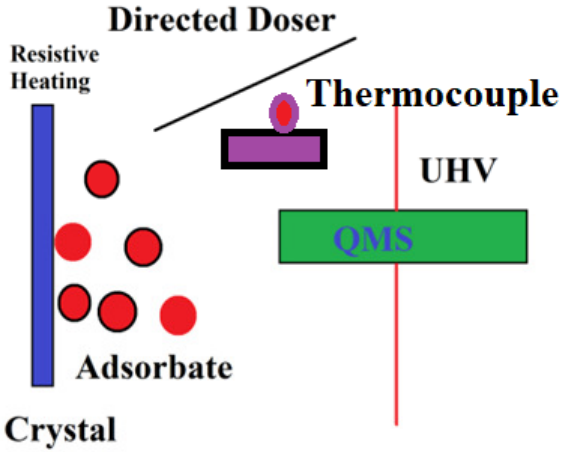
2 PC optical Layout



2 PC set up

Future plans- Surface Science Experiment

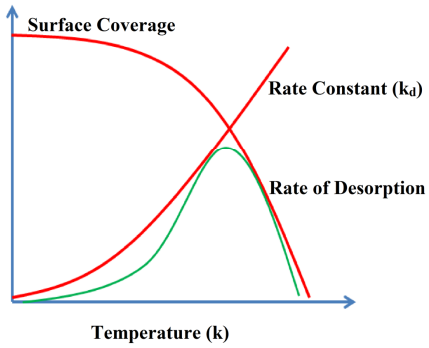
Temperature Programmed Desorption (TPD)



TPD set up

Temperature ramp,

$$\beta = \frac{dT}{dt} = constant$$



Idealized TPD peak

β is in range between 1 to 100 Ks^{-1}

Ref-Attard, Gary. Surfaces. United Kingdom: Oxford University Press, 1998.

Model Catalytic Surface Preparation

Why Glove Box?

For the favorable formation of
Reverse Micelle
In the water free atmosphere.

Glove Box of Chemical Dynamics Lab

Model Catalytic Surface Preparation

Why Spin Coater?

To prepare the monolayer on the support surface

Spin Coater of Chemical Dynamics Lab