서울시립대학교 UNIVERSITY OF SEOUL

Yoo group
Computational Catalysis & Materials Design Lab

Effect of Strain on Ru Surfaces for Ammonia Synthesis Based on Density Functional Theory Calculations

Jaemin Lee, Kyung Jae Min, Seong Cheol Park, Woojin Shin, Sangkyung Lee, Ja Yun Lee, and Jong Suk Yoo*

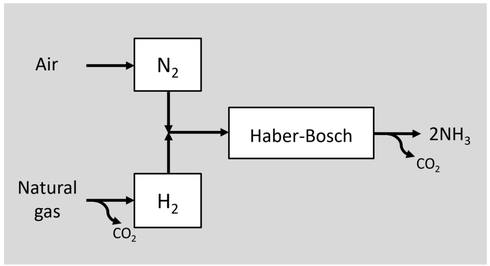
Department of Chemical Engineering, University of Seoul, Seoul, Korea

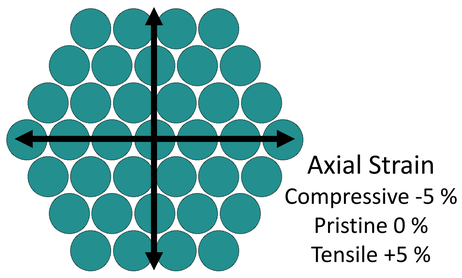
jsyoo84@uos.ac.kr

Abstract

One of the most important feedstocks is ammonia (NH_3), which plays the role of carbon free energy carrier. The conventional Haber-Bosch process has been used for the industrial production of ammonia, but its operation under relatively high temperature and pressure contributes to various environmental issues. Thus, recent investigations for ammonia synthesis under more mild and green conditions are emphasized. In this study, we examine the thermodynamic and kinetic properties of ±5% strained surfaces by using DFT to rationalize the effect of strain on Ru for the enhancement of ammonia production.

Introduction





- Due to the harmful environmental issues of Haber-Bosch process, NH_3 production under more ambient condition is desirable.
- As the stain of catalyst can tune the adsorption energy of intermediates, the performance of catalyst can be subsequently improved by strain.

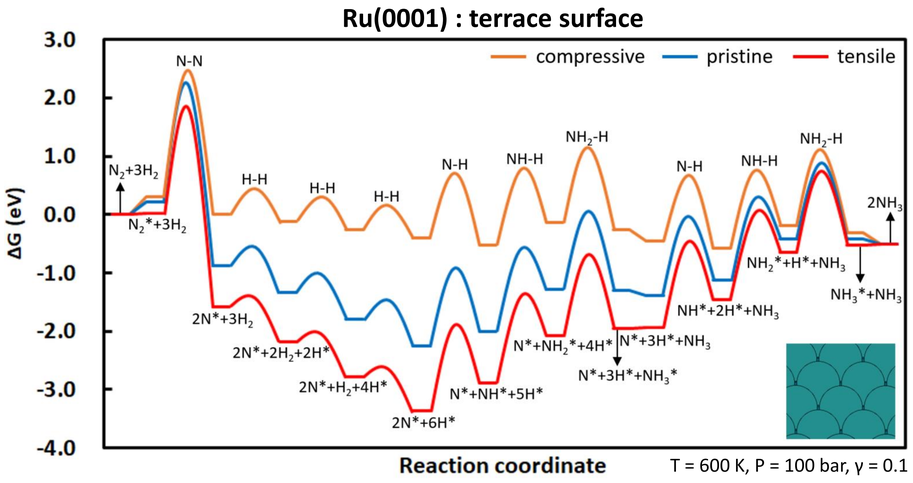
Computational Methods

- VASP software package
- RPBE functional (GGA)
- 2×4×1 for Ru(0001) and 6×4×1 for Ru(10$\bar{1}$0) Monkhorst-Pack *k*-point mesh
- Energy cutoff of 500 eV
- EDIFF of 1×10^{-5} eV and EDIFFG of 0.03 eV/Å

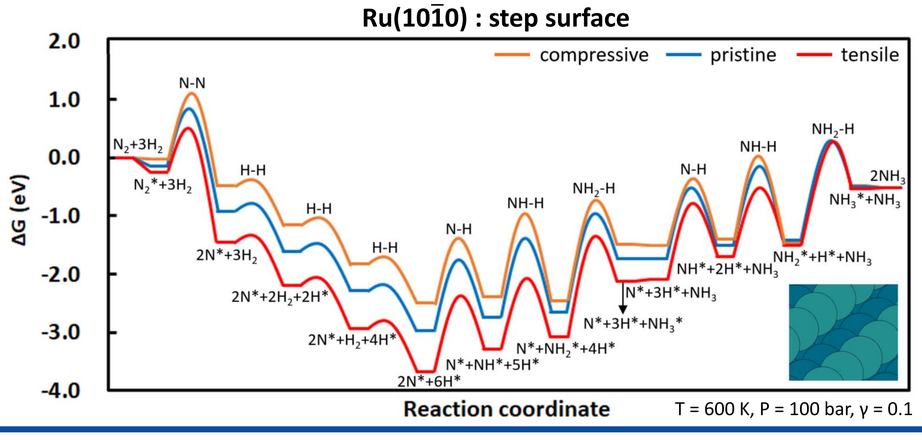
Gibbs Free Energy Diagram

The strained surfaces at terrace and step surface

Ru(0001) : terrace surface



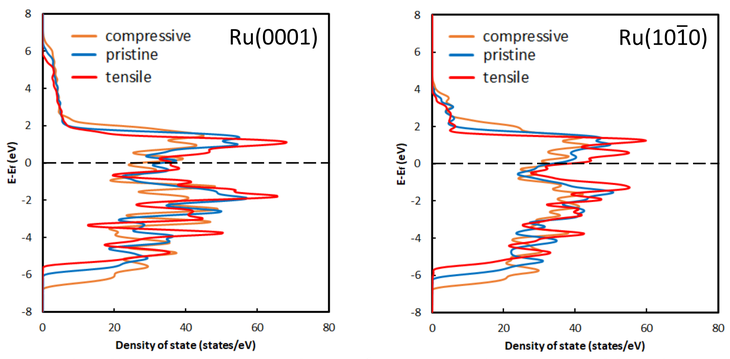
Ru(10$\bar{1}$0) : step surface



- The further the distance of surface atoms is, the stronger the adsorption energies of intermediates.
- At more tensile surface, N_2 and H_2 are easily dissociated, however, the barrier of NH_x hydrogenations become higher.
- The adsorption and activation energies are more affected by strain on step surfaces than terrace surfaces.
- Rate determining step (RDS) of step surfaces may be either NH_2 hydrogenation or N_2 dissociation.

Density of State Analysis

DOS of strained surfaces

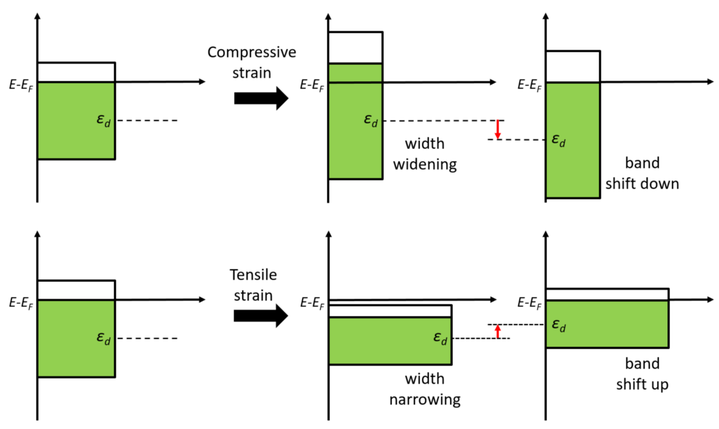


Ru(0001)	Strain (%)		
	-5	0	+5
d-band center $_{(-10,10)}$ [eV]	-1.53	-1.34	-1.19
d-band width $_{(-10,10)}$ [eV]	2.82	2.50	2.24

Ru(10$\bar{1}$0)	Strain (%)		
	-5	0	+5
d-band center $_{(-10,10)}$ [eV]	-1.74	-1.58	-1.44
d-band width $_{(-10,10)}$ [eV]	3.05	2.75	2.50

- As the distance between the surface atoms increases, *d*-band center becomes closer to the Fermi level(E_f) and *d*-band width decreases.

Schematic Diagram of the Change of *d*-band Width and Center upon Strain

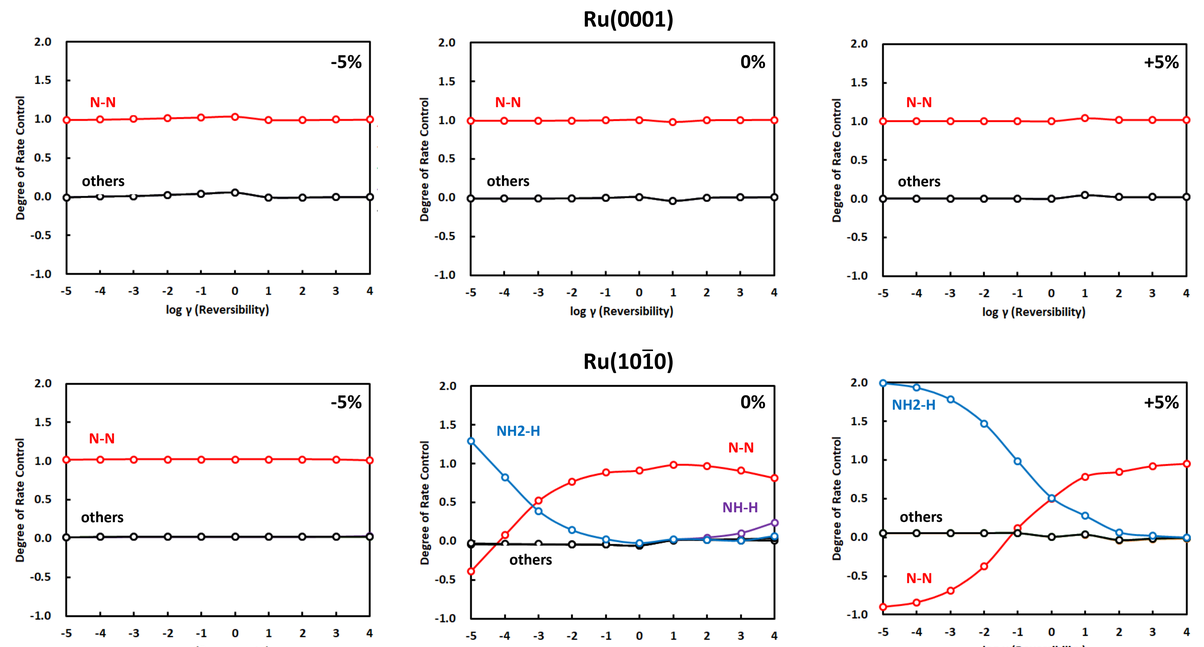


- When compressive strain is applied, the *d*-band is widened shifting *d*-band downward, therefore the *d*-band center shifts further from E_f to preserve band filling. As a result, increased filling of antibonding state weakens bond strength of adsorbates.
- However, when tensile strain is applied, the *d*-band becomes narrower shifting *d*-band upward, therefore adsorption strength becomes stronger.

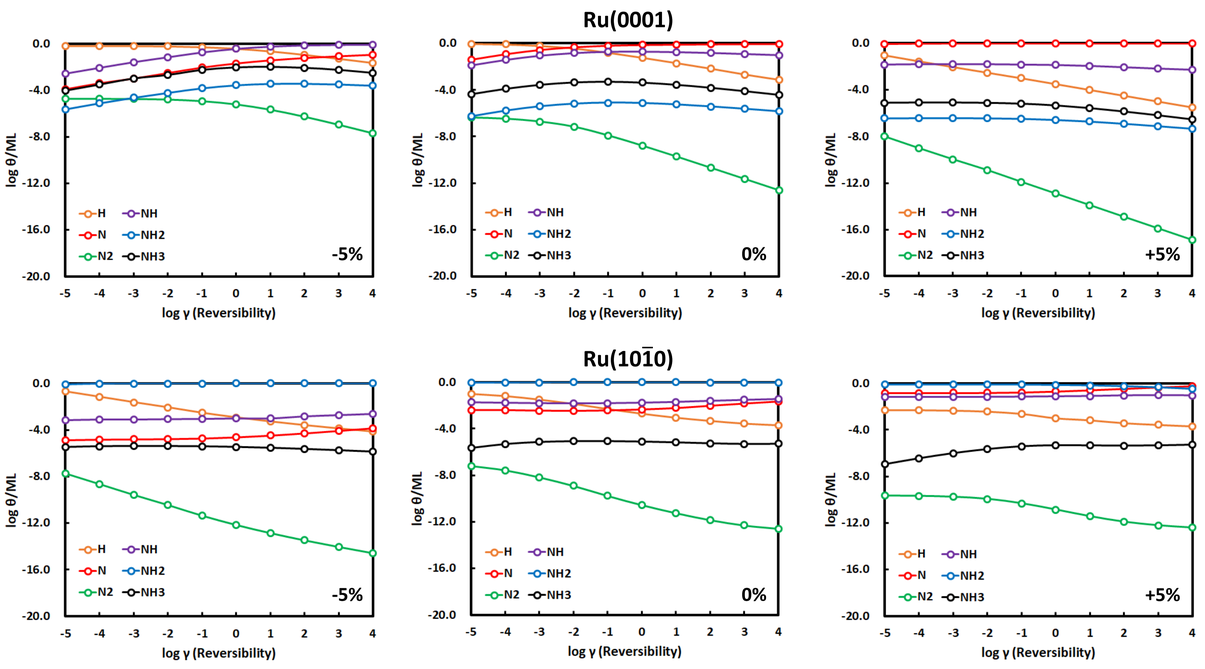
Microkinetic Modeling

Rate Determining Step (RDS) Determination

1. Degree of rate control (DRC) against the reversibility of strained surfaces



2. Coverage (θ) of intermediates against the reversibility of strained surfaces



- When the reversibility increases, the coverage of N_2 is rapidly reduced, resulting in the change of rate and DRC of each step.
- Since the barrier of N_2 dissociation is smaller and of NH_2 hydrogenation is bigger at more tensile surface, DRC of NH_2-H becomes the biggest in condition that the reversibility values are negative.

Conclusions

- The adsorption and activation energies on strained Ru surfaces are affected by strain.
- Due to the increase of distance between surface atoms, the *d*-band width decreases and *d*-band center become closer to E_f. Therefore, the adsorption energies become stronger through the reduction of antibonding below E_f.
- Based on DRC analysis, the RDS of step surfaces is determined as NH_2 hydrogenation on both pristine and tensile surfaces at extremely negative γ.