Modeling the Ammonia Decomposition Reaction for Hydrogen Production

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Motivation

Ammonia as a hydrogen carrier in a “hydrogen economy”
- Ammonia is widely produced (100 million metric tonnes per year)
- Compatible with the current infrastructure
- Can be catalytically decomposed on-board to create CO free H2 for a fuel cell

Rational Catalyst Design

- Microkinetic models are an inexpensive and efficient way to screen catalysts
- Insights gained from models will help develop better catalysts

Microkinetic Modeling

Microkinetic Analysis
- Modeling overall reaction in terms of elementary reactions
- No assumptions concerning the kinetically significant elementary steps,
or most abundant reaction intermediate

The ammonia decomposition reaction consists of 12 elementary reaction steps

• N-N interaction parameters were calculated through DFT

Interaction Parameters

The Vienna Ab-initio Simulation Package (VASP) was used to calculate heats of chemisorption as a function of adsorbate coverages from 1/9 to 1 monolayer (ML)
- The slope of the heat of chemisorption as a function of coverage is called the interaction parameter (\(\beta\))

Conclusion

- A library of thermodynamically consistent microkinetic models has been developed for the first time to describe the chemistry on various single metals
- Nitrogen-nitrogen adsorbate interactions were estimated using VASP for metals with high nitrogen coverages and these interactions were included in the microkinetic models
- A linear correlation was used to estimate the heat of nitrogen chemisorption as a function of nitrogen coverage
- Interactions reduced the amount of nitrogen adsorbed on the surface
- Increased the amount of surface hydrogen

Interaction parameters were calculated for different adsorbates on ruthenium
- Strength of interactions are a function of atomic radius
- N-N interactions are much stronger than H-H interactions

N-N and H-H interaction parameters were calculated for a number of metals
- The averages and standard deviations are shown in the figure to the right

Surface Coverages and Sensitivity Coefficients (SC) without Interactions

Surface Coverages and Sensitivity Coefficients were calculated for different adsorbates on ruthenium
- Strength of interactions are stronger than H-H interactions

Surface Coverages and Sensitivity Coefficients with N-N and NHx-N Interactions

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Microkinetic Modeling

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12 activation energies ~ 12 pre-exponentials
Operating conditions

Activation Energies (E_a) - Bond Order Conservation (BOC)

Low coverage values: temperature programmed desorption (TPD)
Coverage effects: density functional theory (DFT)

Conversions
Surface coverages
Reaction rates

Pre-exponential factor (s\(^{-1}\)) or
Reaction rates

Pre-exponential Fit to Ruthenium Experimental Data
(Assumed valid for All Metals)

Pre-exponential factor (s\(^{-1}\)) or

Experimental Operating Conditions/Parameters

Diameter = 0.32 cm
Length = 1.0 cm
Pressure = 1.0 atm
Flow rate = 70 sccm
Surface density = 13,100 cm\(^2\)/cm\(^3\)

Model Inputs

Activation Energies (E_a) - Bond Order Conservation (BOC)

Atomic heats of chemisorption (Q_h, Q_N)
Gas phase molecular bond energies
Activation energies for all 12 elementary steps

Pre-exponents Fit to Ruthenium Experimental Data
(Assumed valid for All Metals)

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- A linear correlation was used to estimate the heat of nitrogen chemisorption as a function of nitrogen coverage
- Interactions reduced the amount of nitrogen adsorbed on the surface
- Increased the amount of surface hydrogen
- Increased the catalytic activity
- VASP calculations were used to confirm the validity of a DFT-BOC hybrid method
- A DFT-BOC hybrid method does well at approximating the NHx-N interactions and is computationally inexpensive

Conclusions

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- A DFT-BOC hybrid method does well at approximating the NHx-N interactions
- This method was used to calculate NHx-nitrogen interactions for metals in the microkinetic library

Future Work

- Complete microkinetic model development
- Calculate nitrogen – hydrogen adsorbate interactions using VASP
- Compare microkinetic models to experimental data
- Predict activity for more complex catalytic surfaces (bimetallics, surface defects, etc.) in order to develop higher activity catalysts using microkinetic modeling

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