Mechanistic Insights into Electrochemical Nitrogen Reduction Reaction on Vanadium Nitride Nanoparticles

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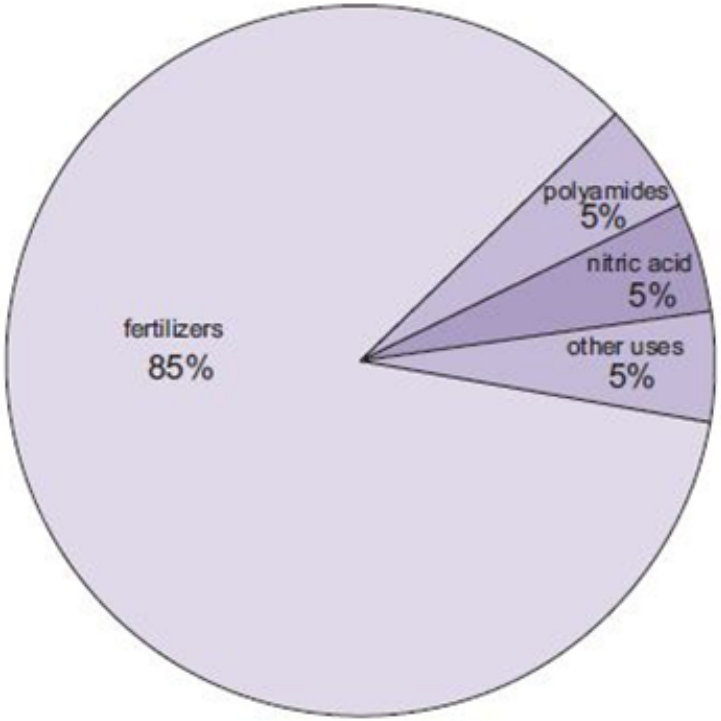
AIChE at Orlando, FL
November 14, 2019

Importance of Ammonia



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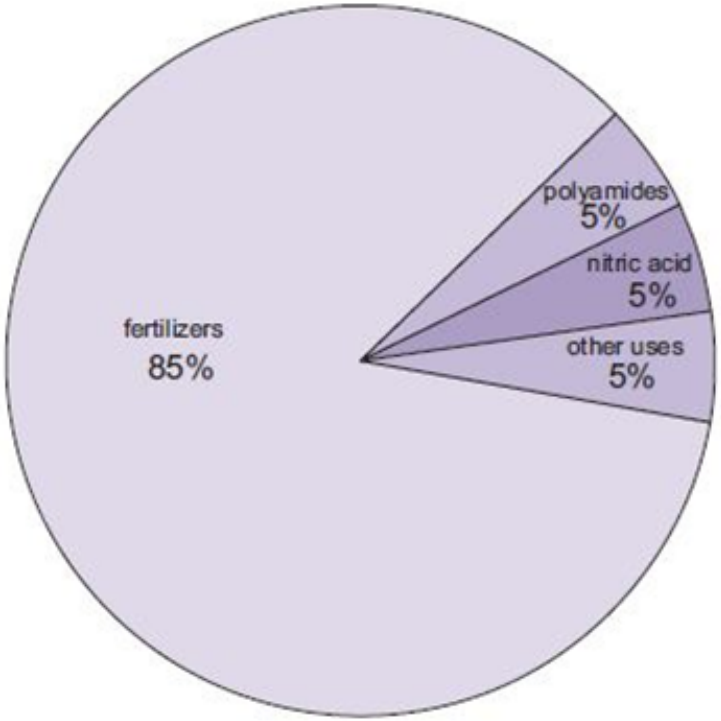

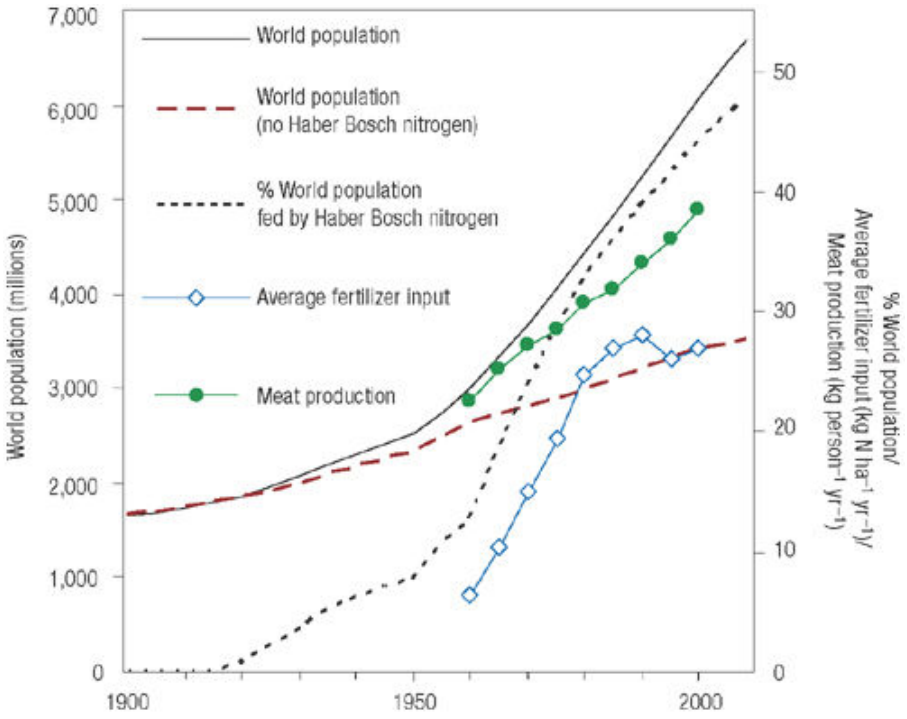

nitrogen fertilizer supported ~27% of the world's population over the past century

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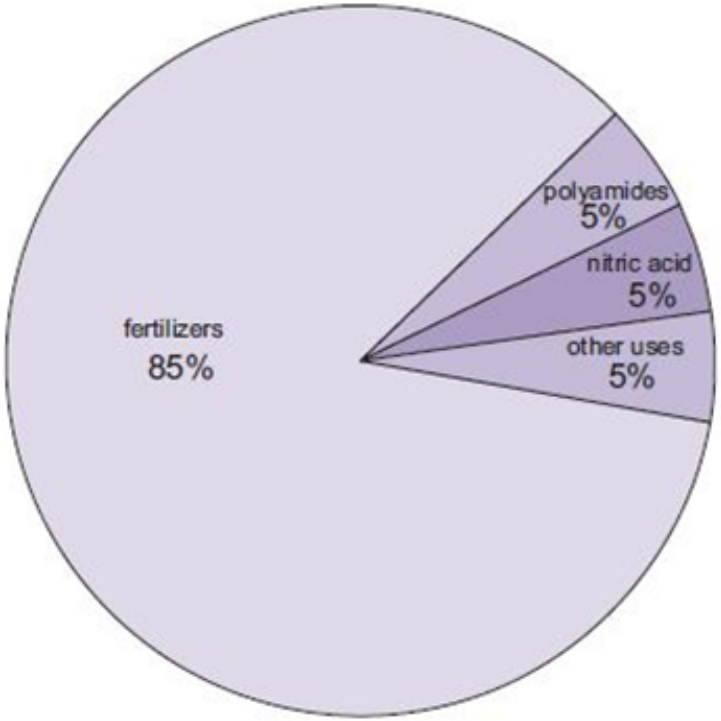

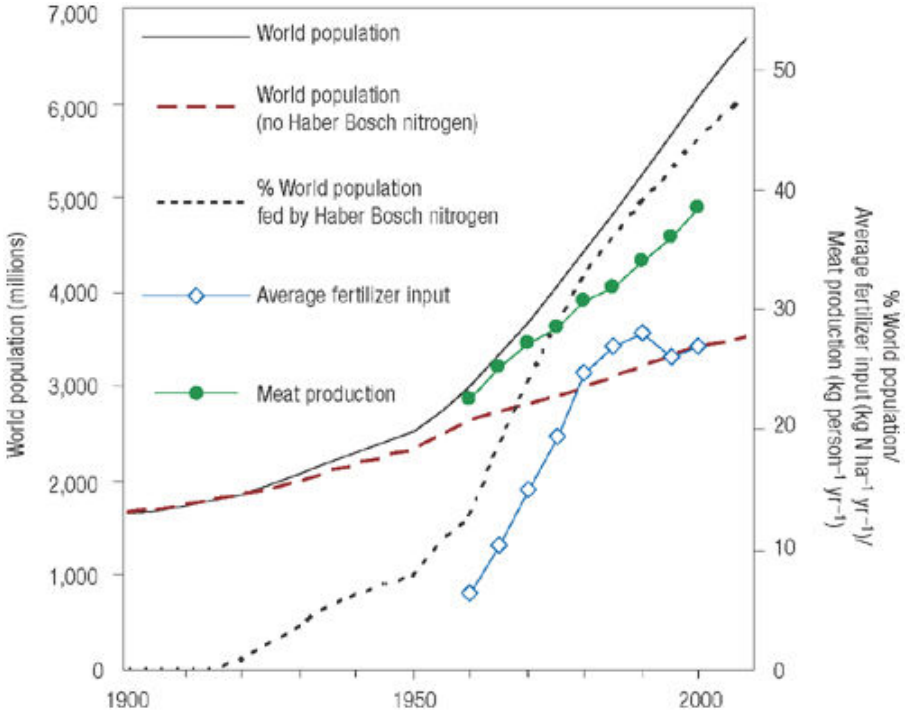

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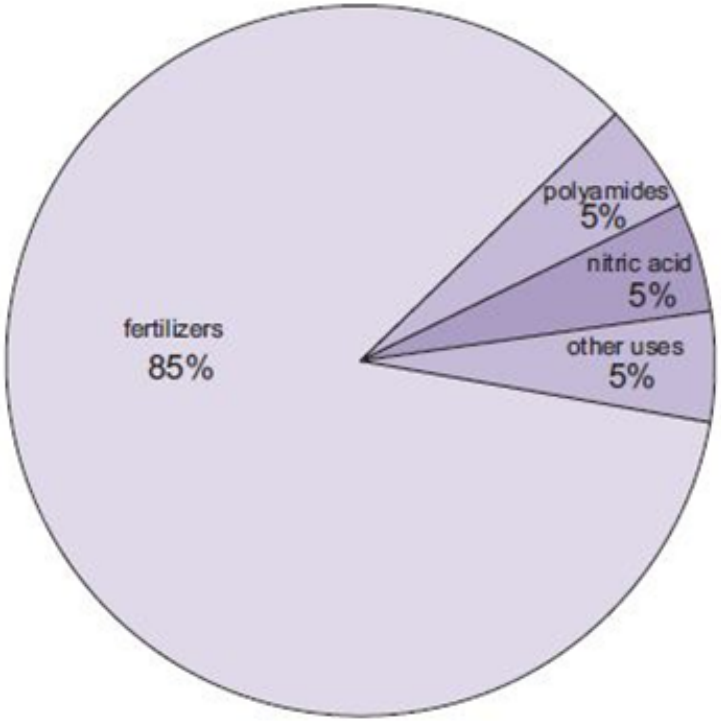

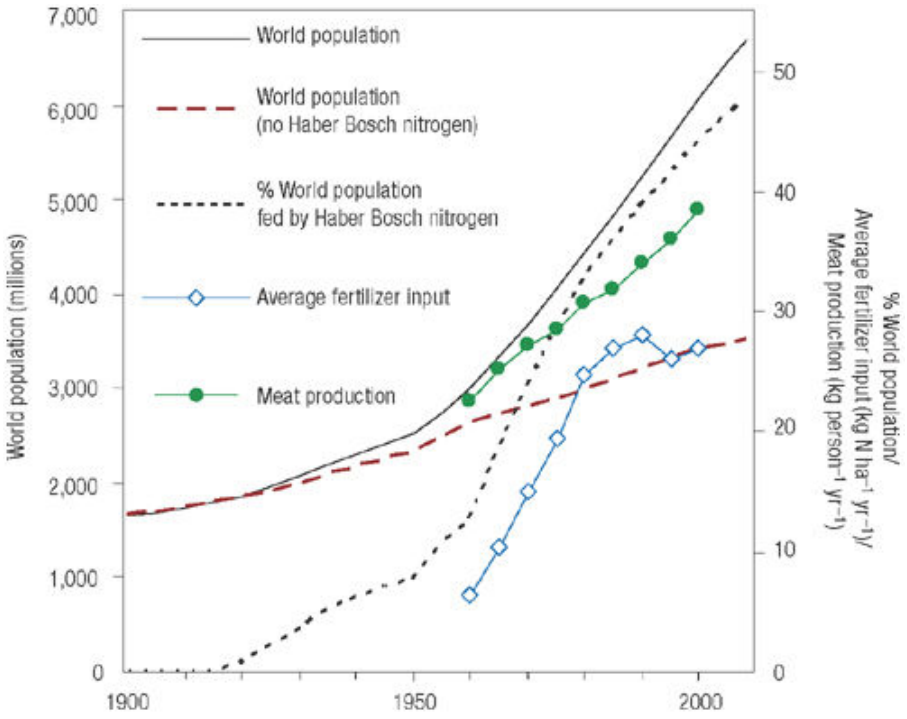

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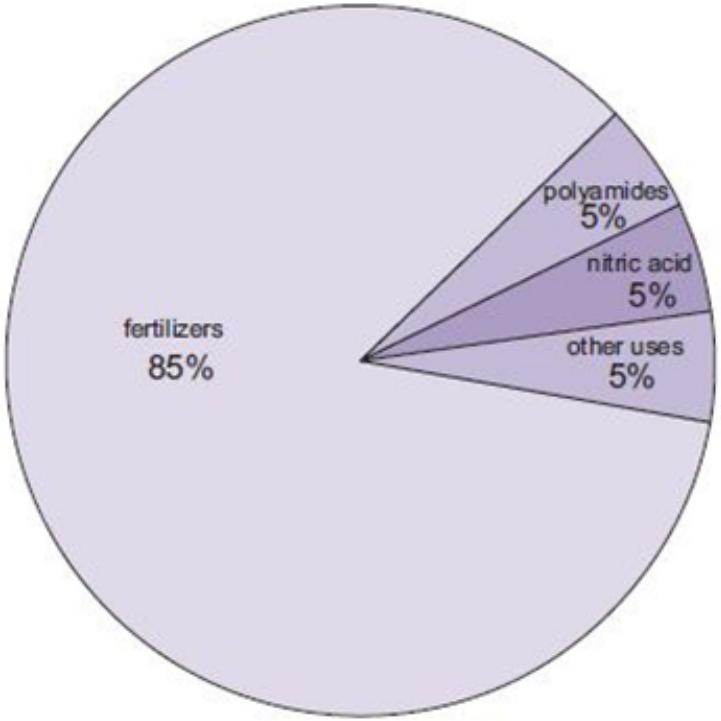

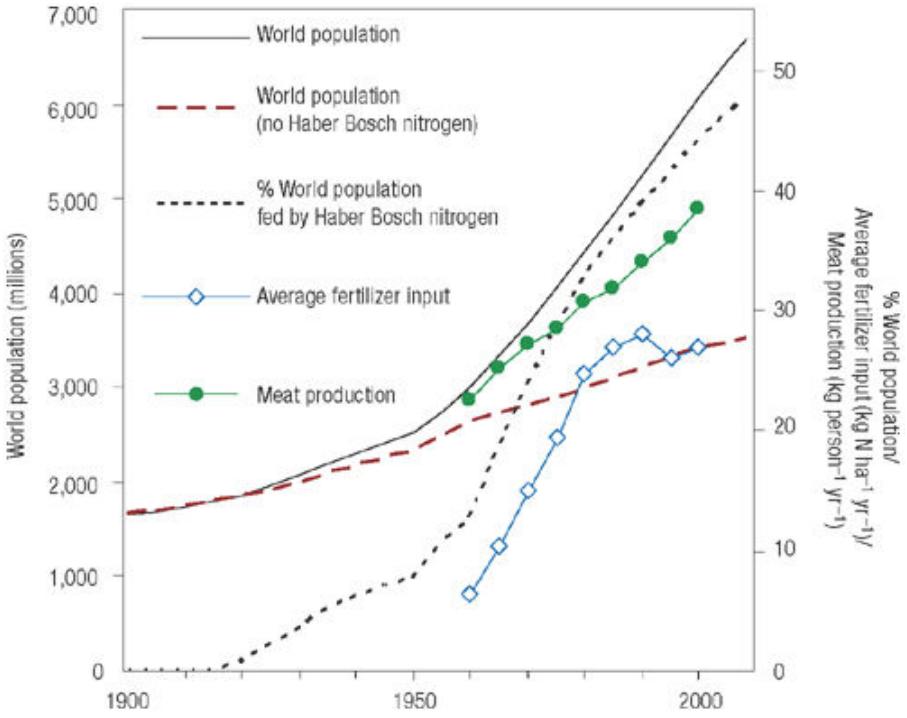

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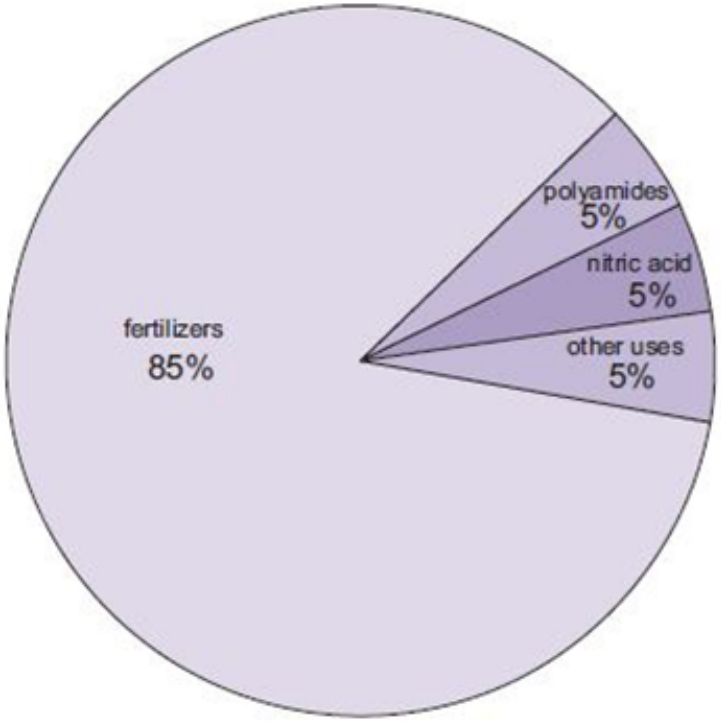

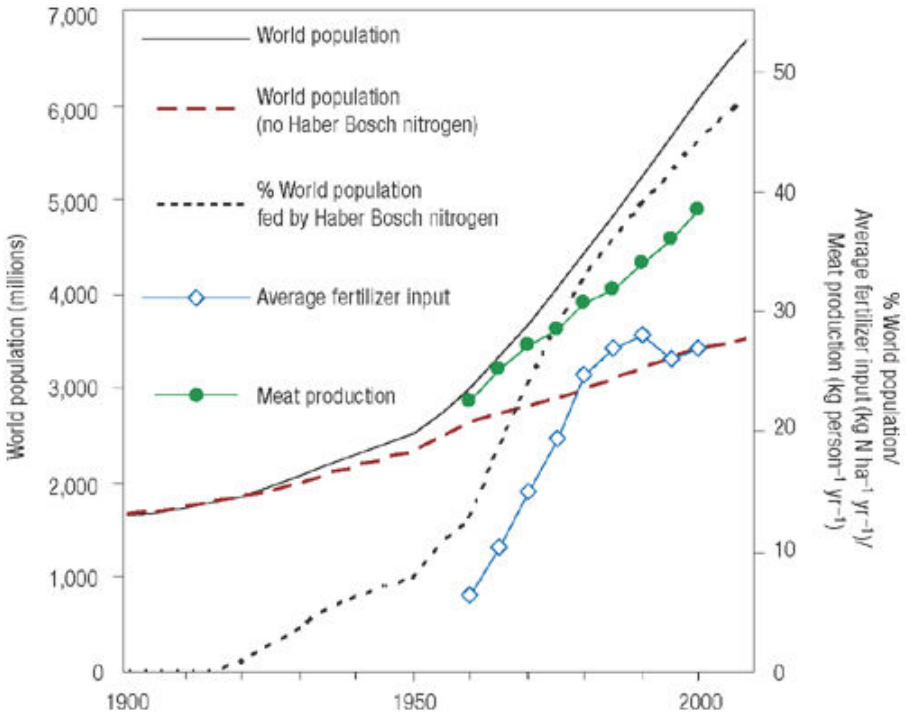

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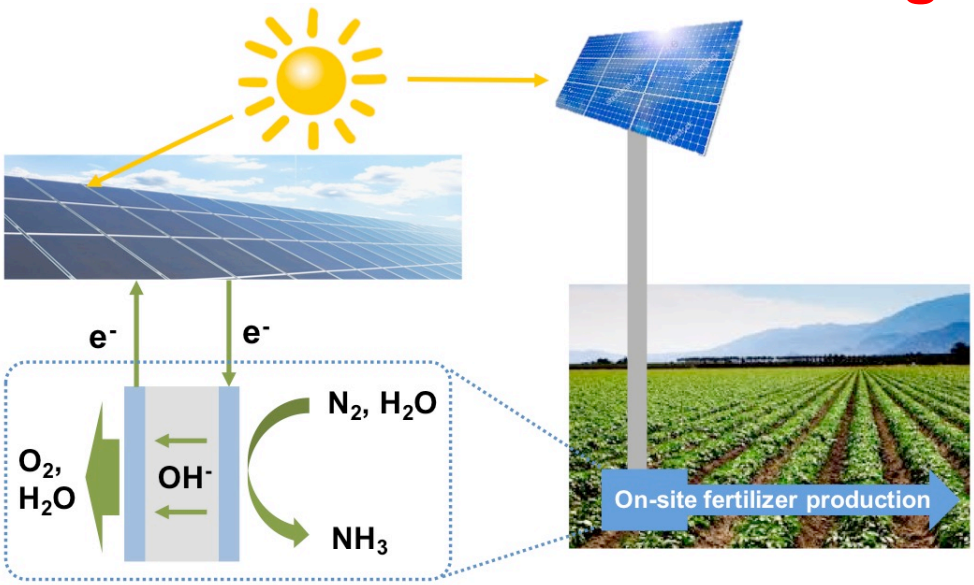
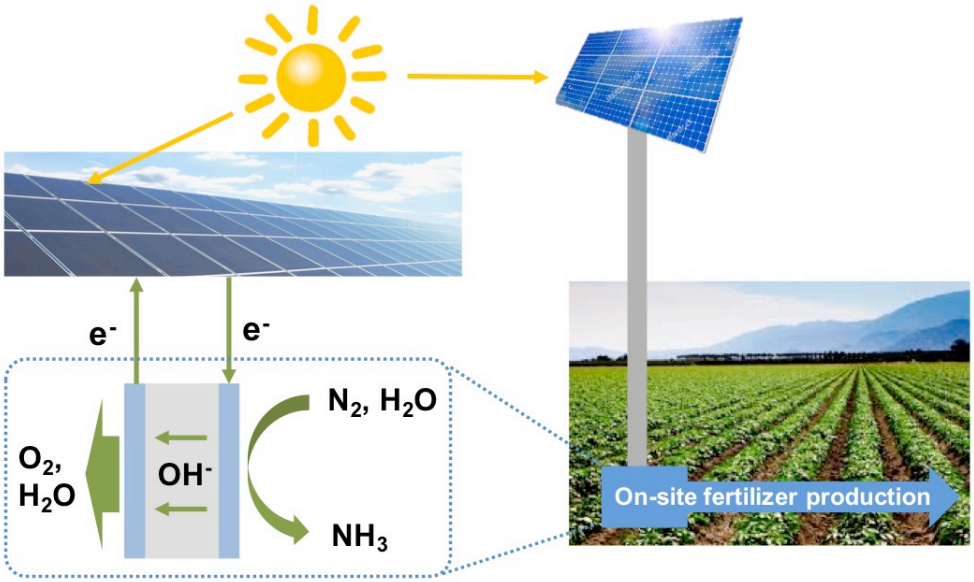
Electrochemical Nitrogen Reduction (ENRR)

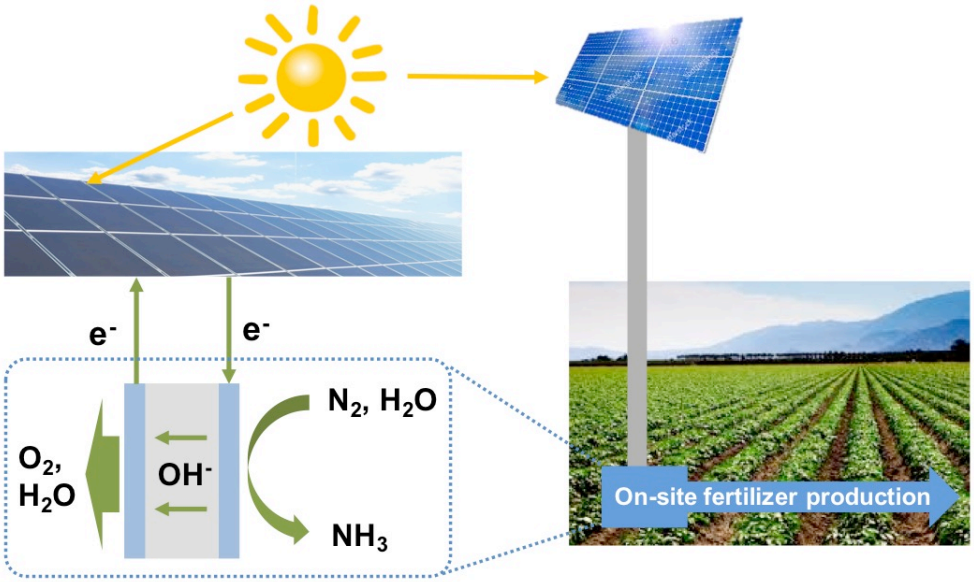


ENRR



1. Renewable energy

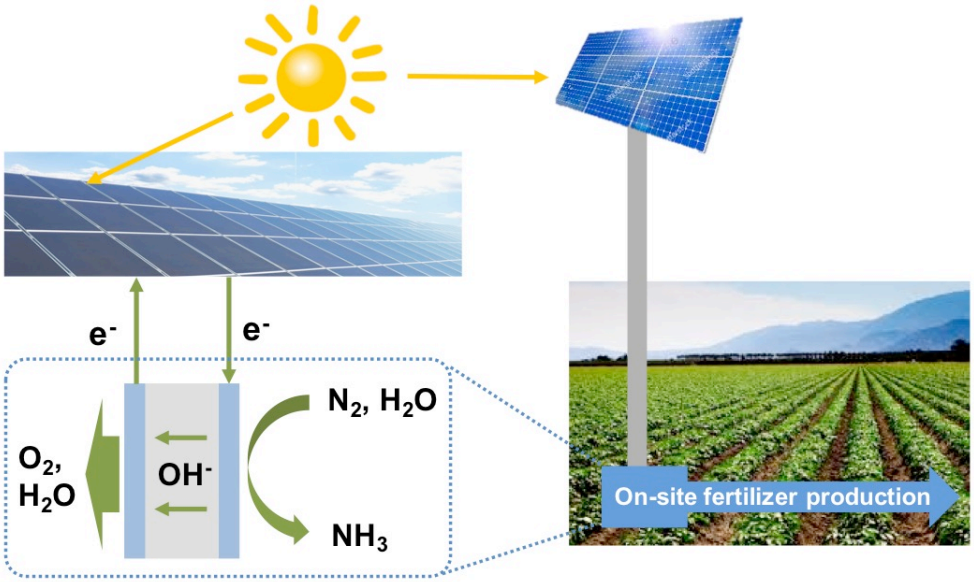
ENRR



1. Renewable energy

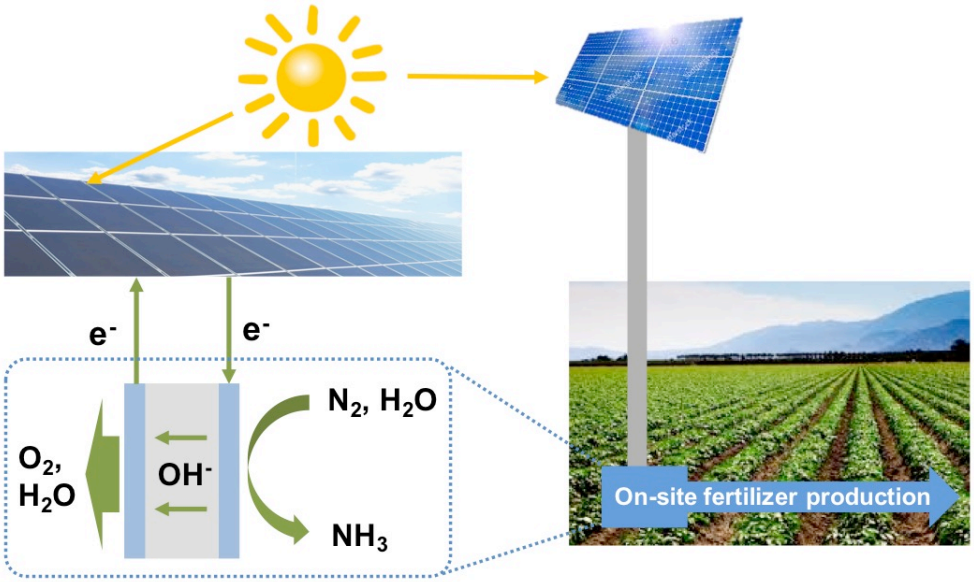
2. Low temperature and pressure

ENRR



1. Renewable energy
2. Low temperature and pressure
3. On-site production

ENRR



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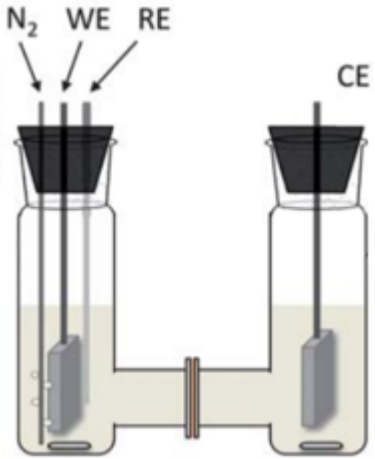
Batch Cell



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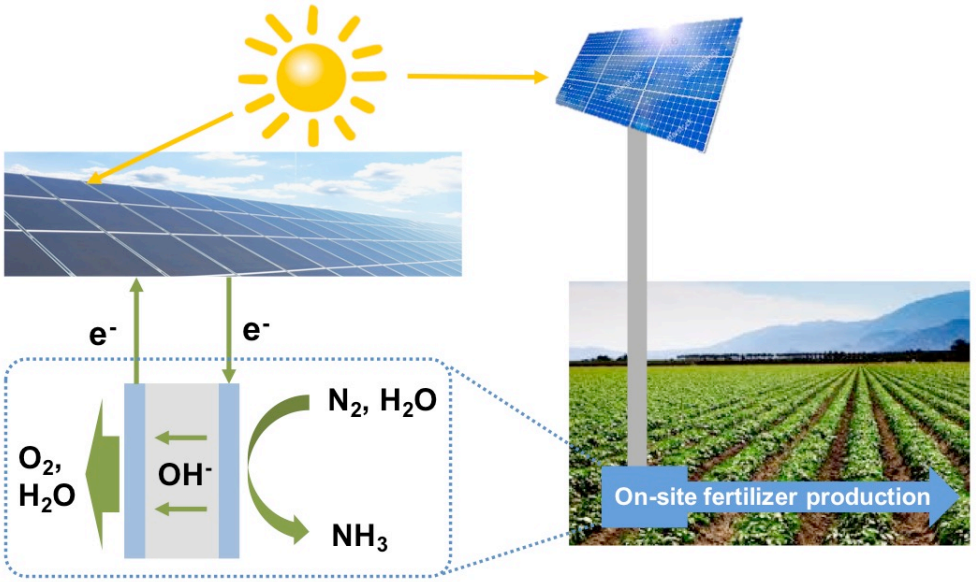

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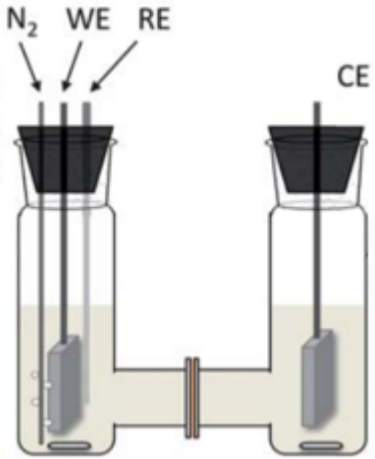

Not suitable for large scale synthesis

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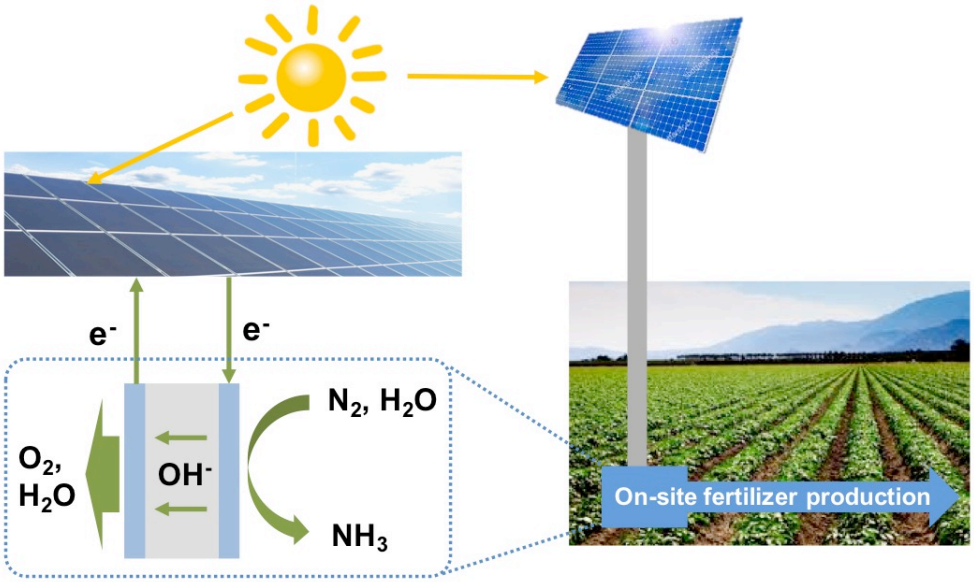

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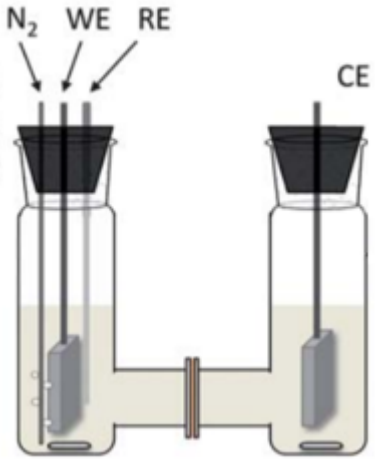

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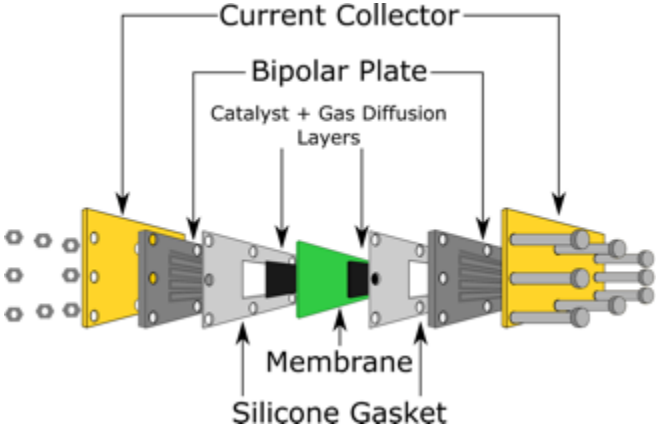
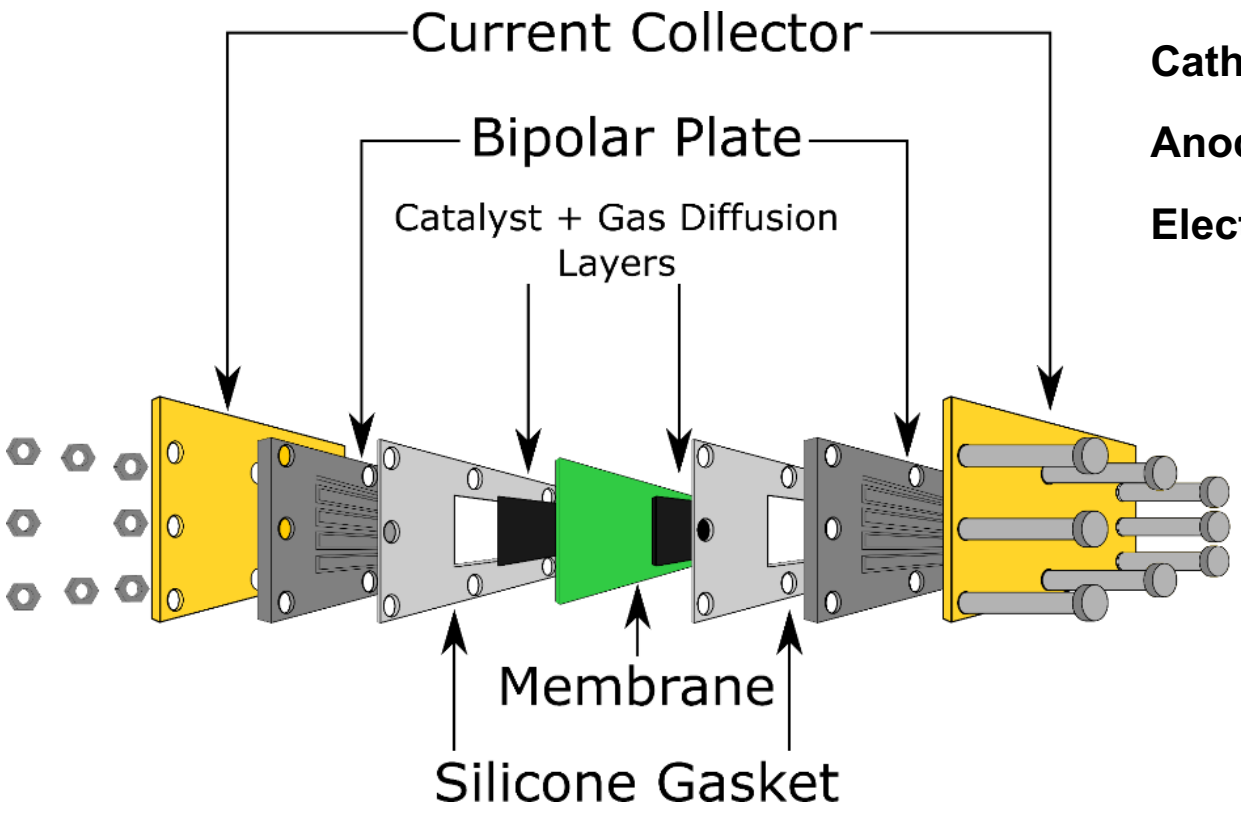
Membrane Electrode Assembly



Easy to scale up

Setup for ENRR



Cathode: 0.5 mg cm^{-2} catalysts (N_2)

Anode: 0.4 mg cm^{-2} Pt (H_2)

Electrolyte: Nafion-211 membrane

Membrane electrode assembly (MEA) configurations provide reliable activity measurements

Transition Metal Nitrides for ENRR

	RS(100)	RS(111)	ZB(100)	ZB(110)
ZrN	75% CE of NH_3 U = -0.76 V	60% CE of NH_3 U = -1.42 V		40% CE of NH_3 U = -1.02 V
NbN	75% CE of NH_3 U = -0.65 V	75% CE of NH_3 U = -1.12 V		Decomposition U = -0.59 V
CrN	100% CE of NH_3 U = -0.76 V	Decomposition U = -0.58 V	Non-catalytic U = -1.11 V	86% CE of NH_3 U = -0.54 V
VN	100% CE of NH3 U = -0.51 V	Decomposition U = -0.85 V	Decomposition U = -0.97 V	Decomposition U = -1.06 V

Abghoui et al. *ACS Catalysis* **2016**, *6*, 635−646

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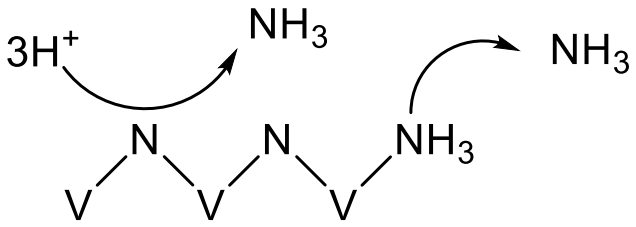
VN Presents Degradation Problem

- **NH_3 could be formed from VN degradation**



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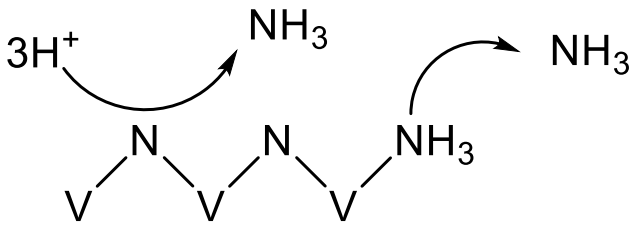

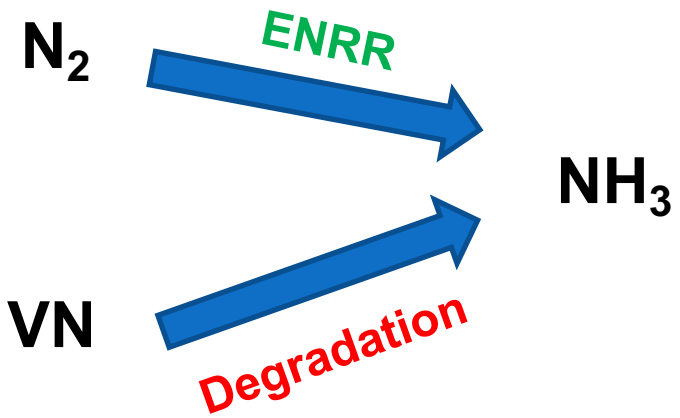

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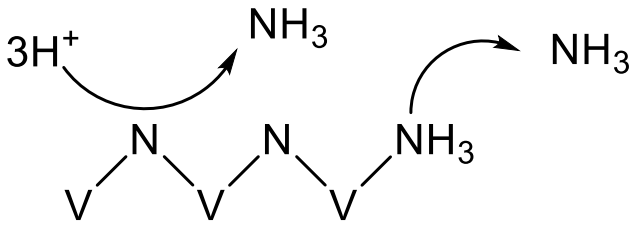

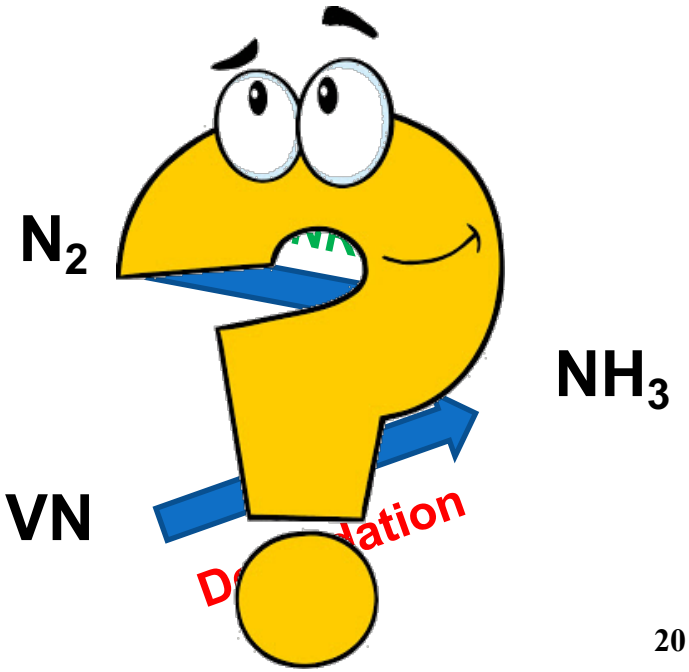

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Quantification of Ammonia

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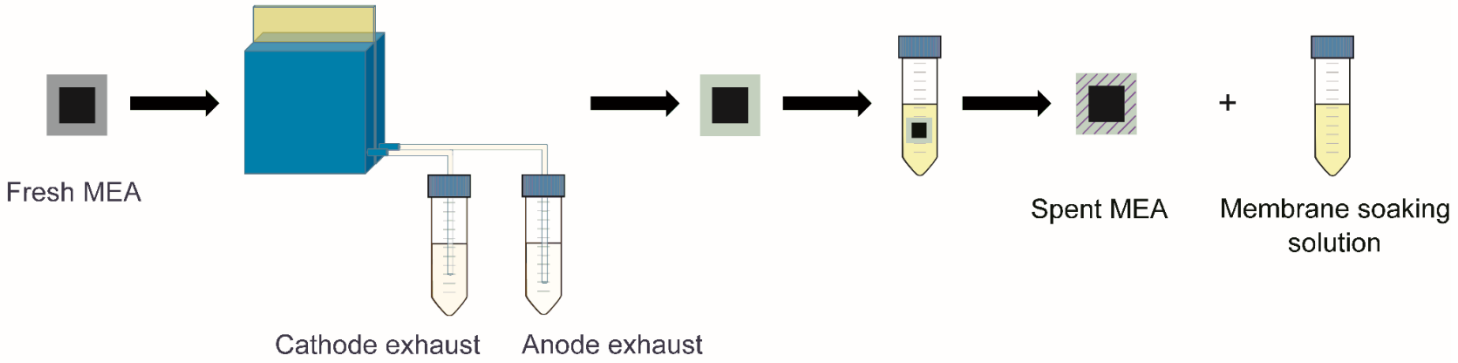

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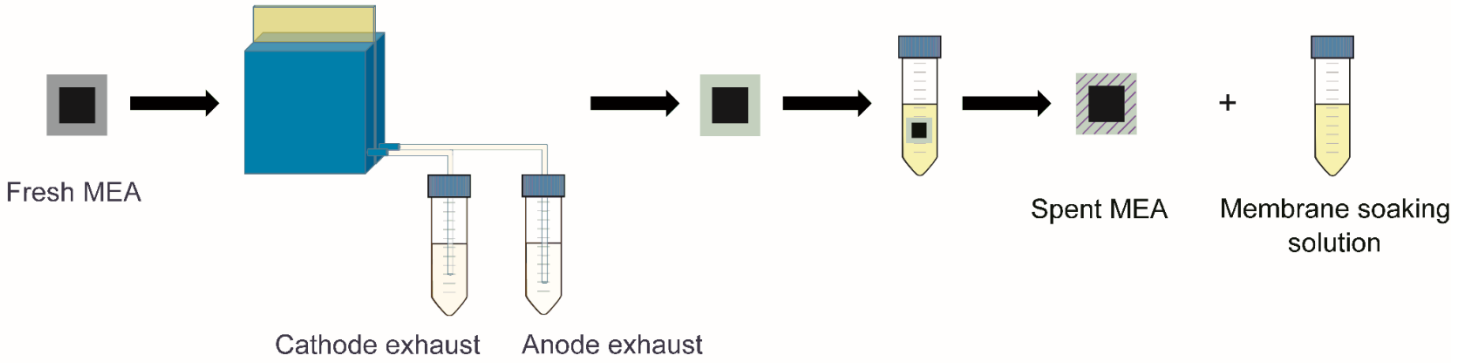
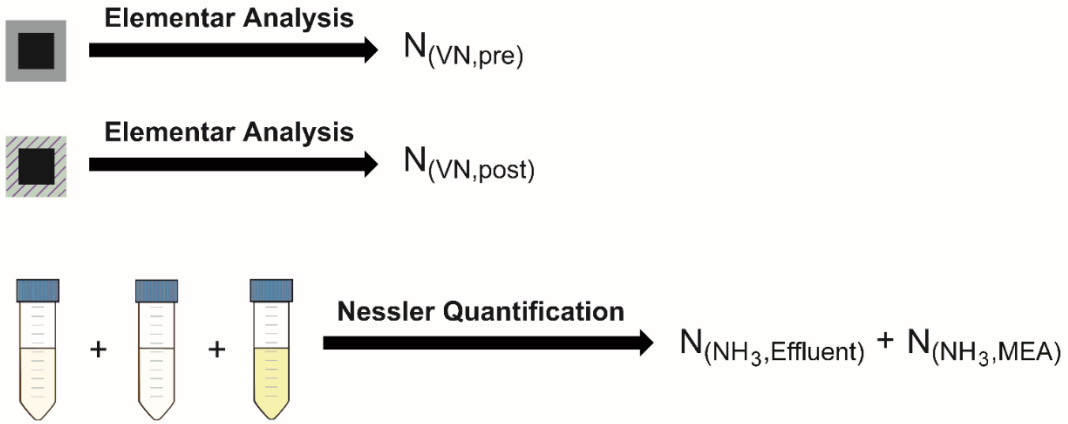


II. Sample Analysis



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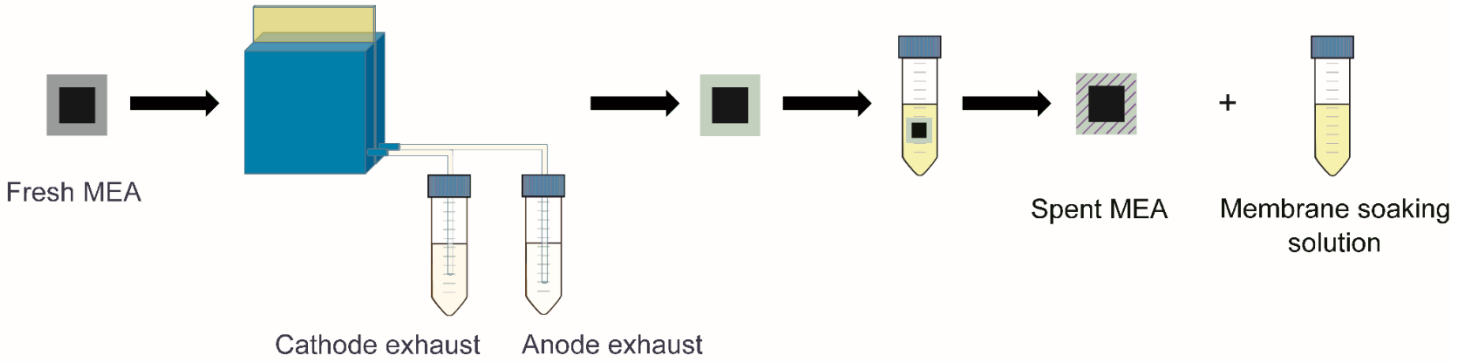
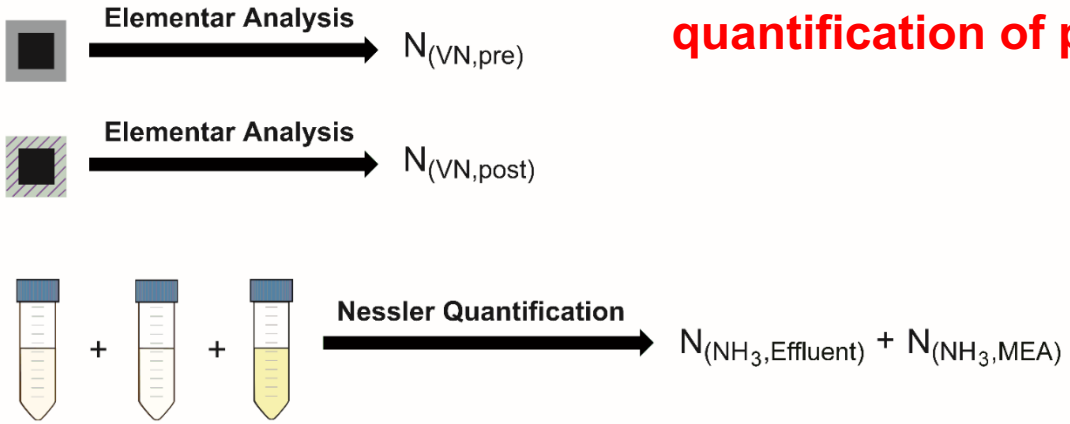


II. Sample Analysis

N mass balance enables the reliable quantification of produced ammonia

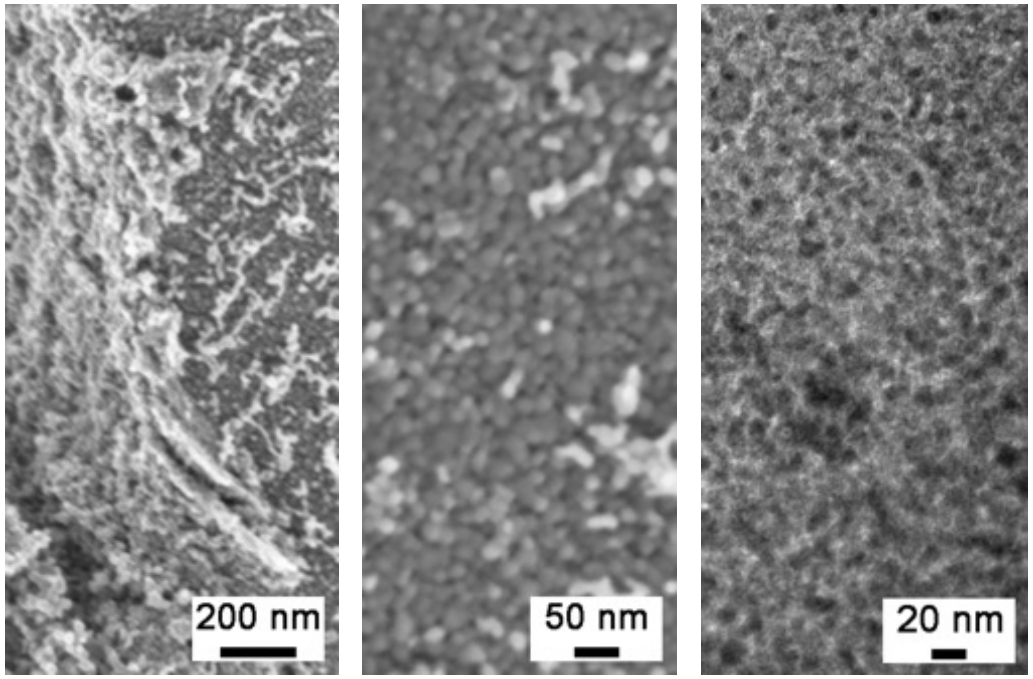


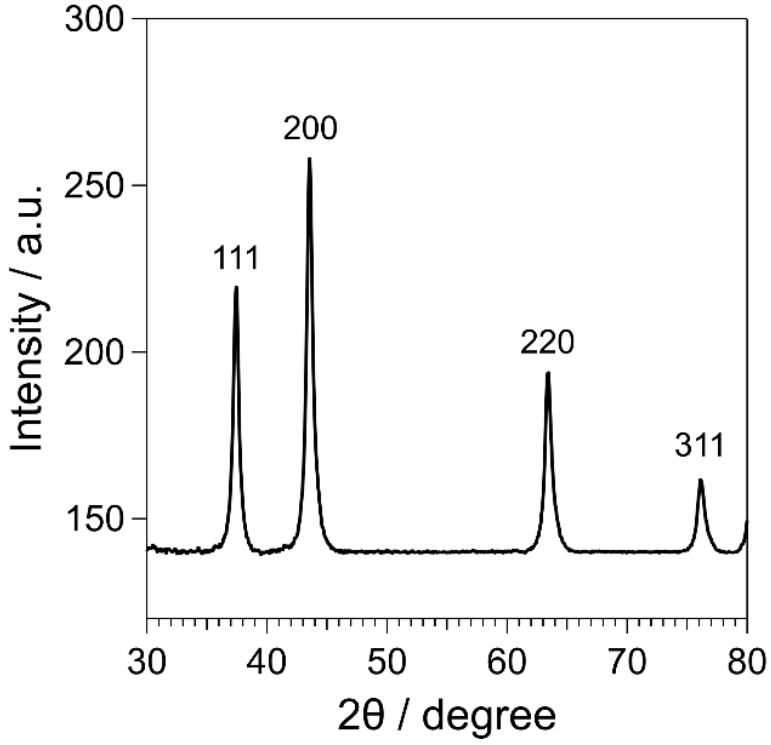
III. Ammonia Quantification

$$N_{(NH_3,ENRR)} = N_{(NH_3,Effluent)} + N_{(NH_3,MEA)} + N_{(VN,post)} - N_{(VN,pre)}$$

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

VN is an Active, Selective and Stable ENRR Catalyst





Particle size: 6 − 15 nm

Cubic VN phase

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

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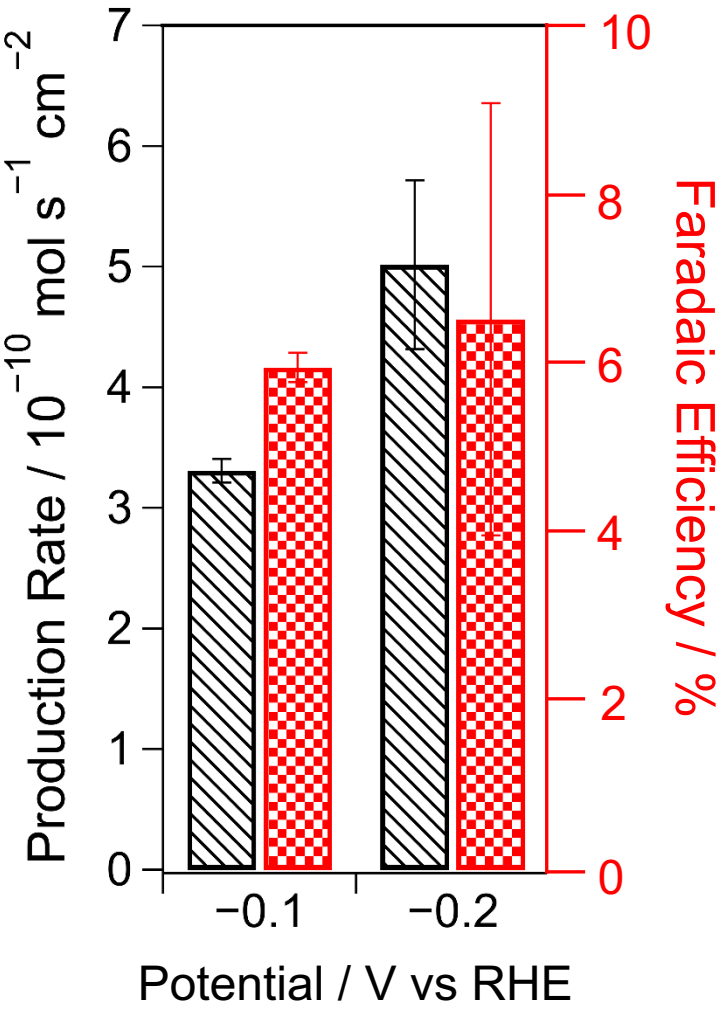

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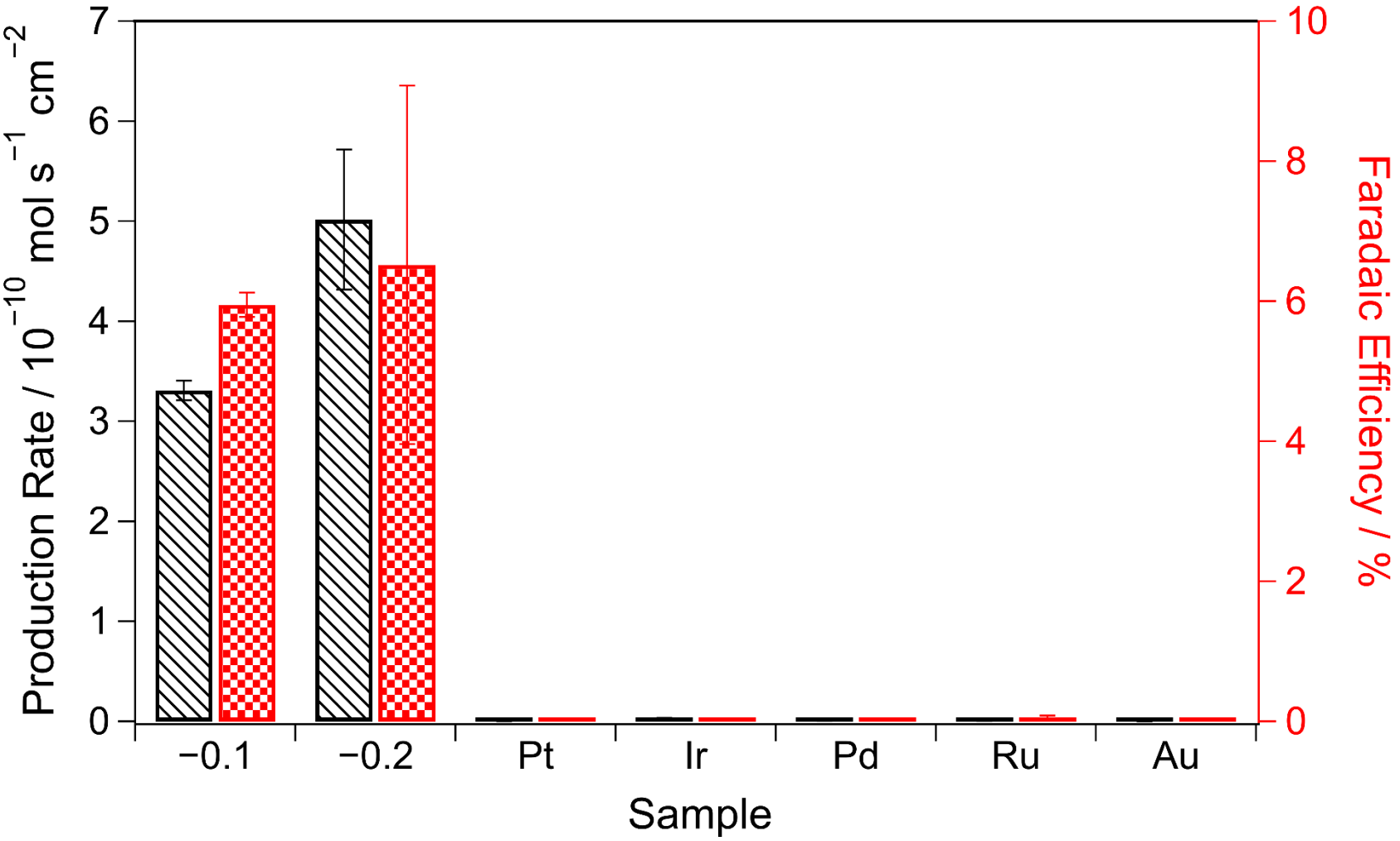

Two orders of magnitude more active and selective than noble metal catalysts

Nash et al. *J. Electrochem. Soc.* **2017**, *164*, F1712−F1716

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

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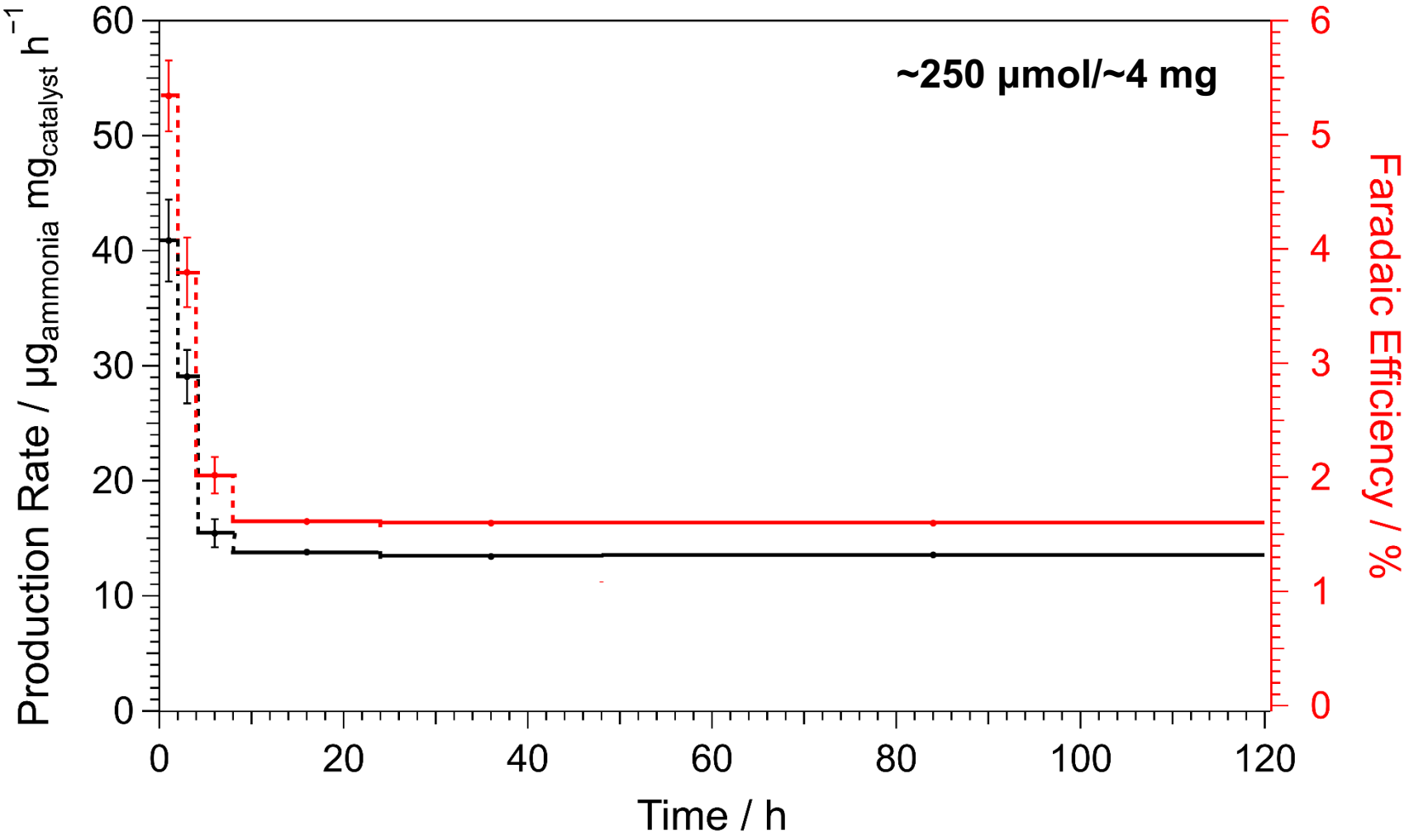
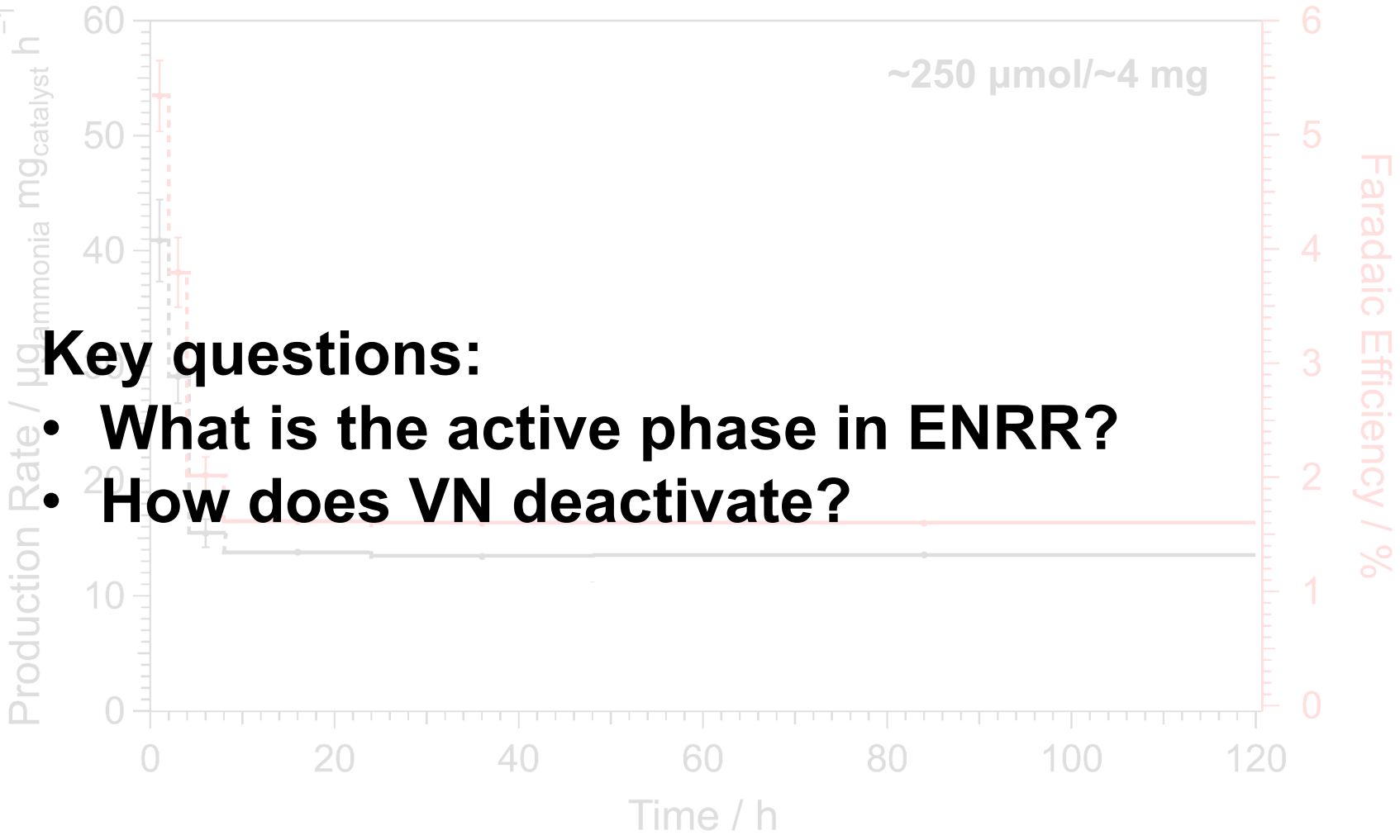


The N content in produced ammonia is about 9.4 times that in the catalysts

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

VN is an Active, Selective and Stable ENRR Catalyst



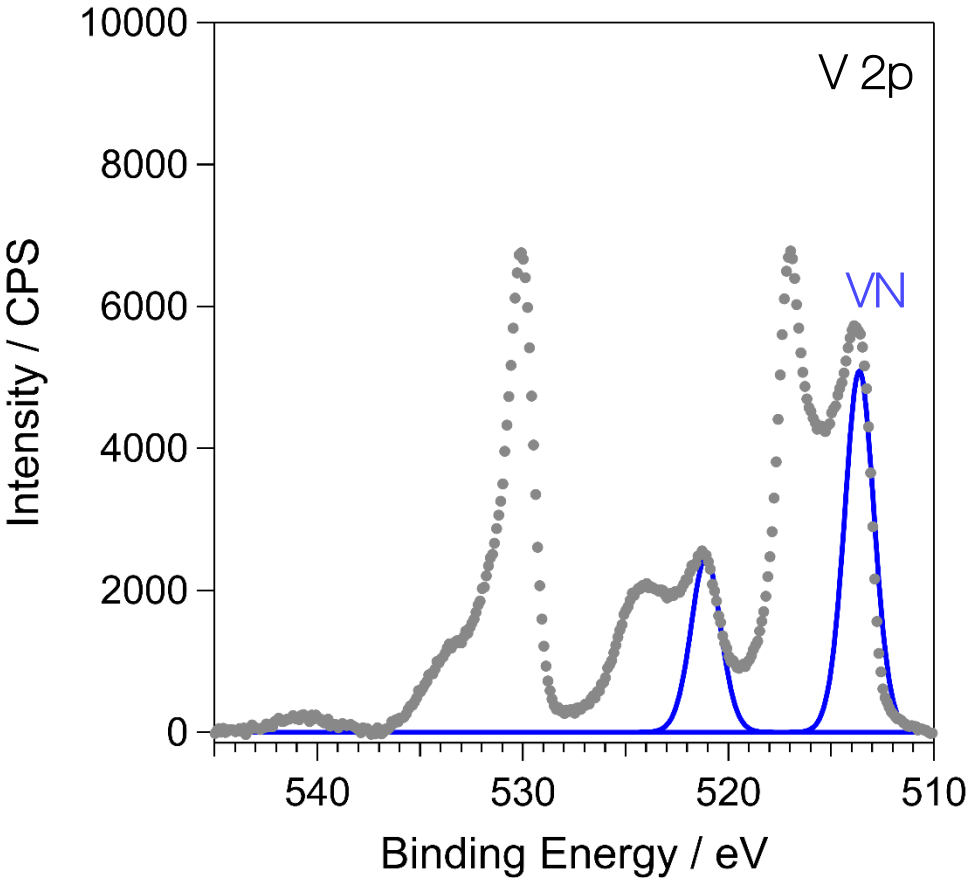
Key questions:

- **What is the active phase in ENRR?**
- **How does VN deactivate?**

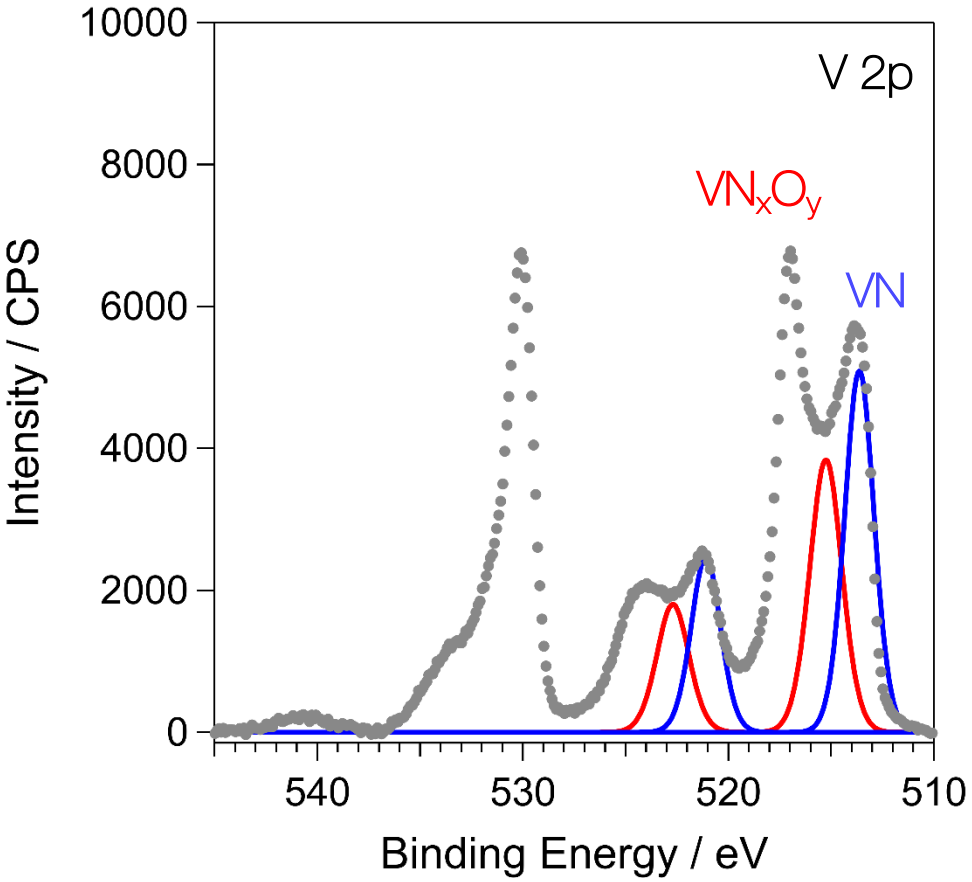
The N content in produced ammonia is about 9.4 times that in the catalysts

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

XPS of VN Catalysts before ENRR



XPS of VN Catalysts before ENRR



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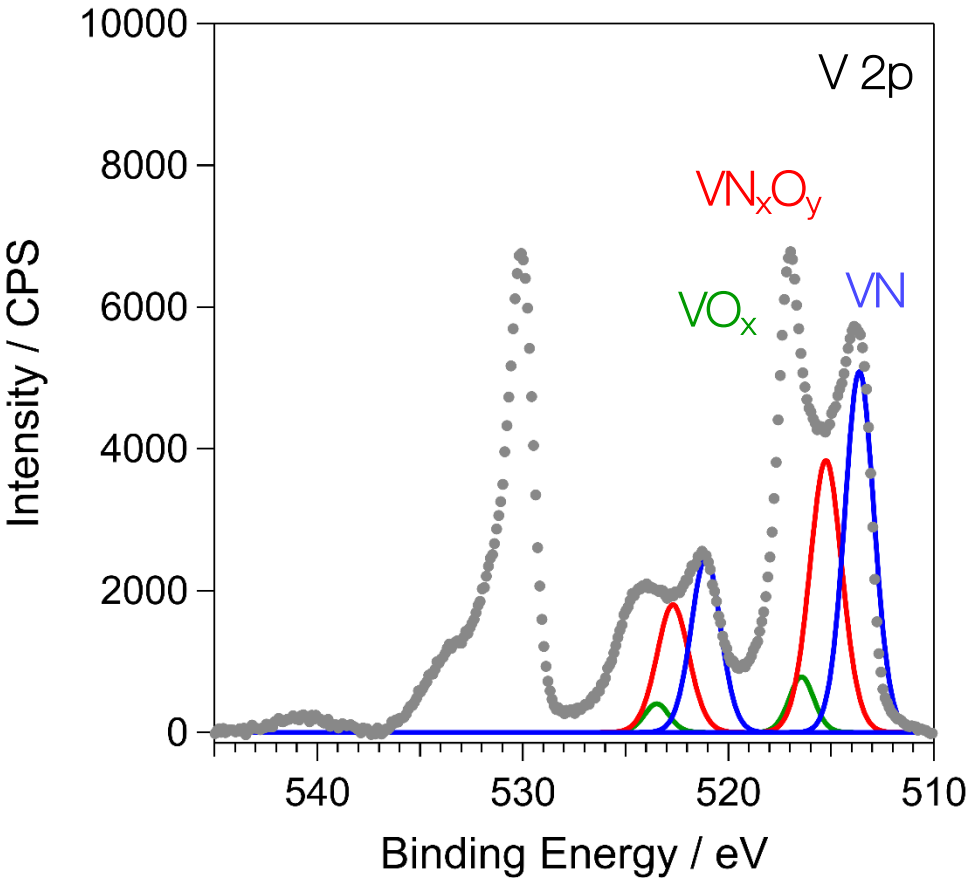

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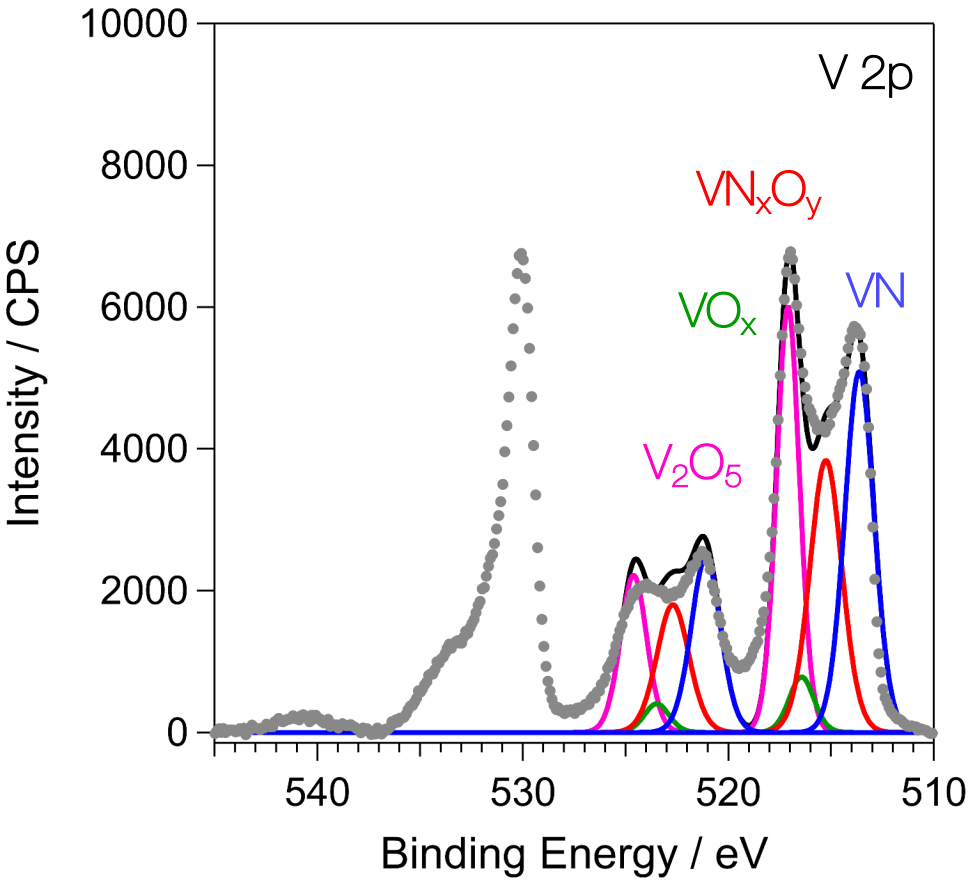

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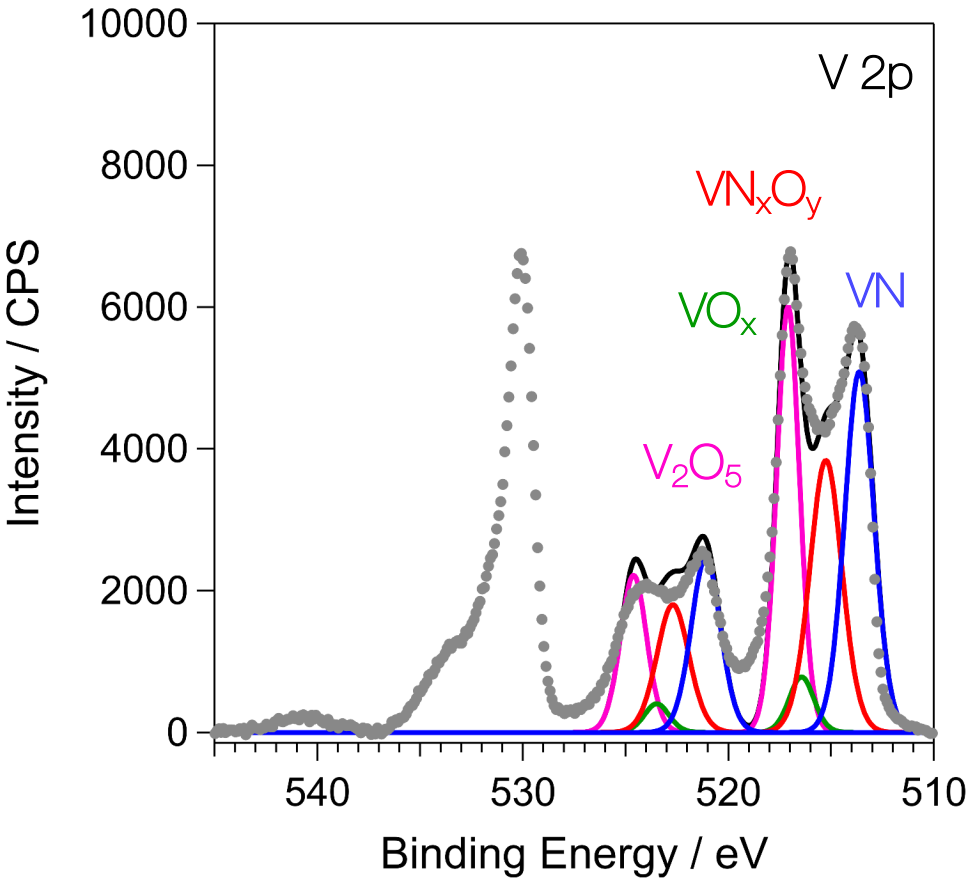
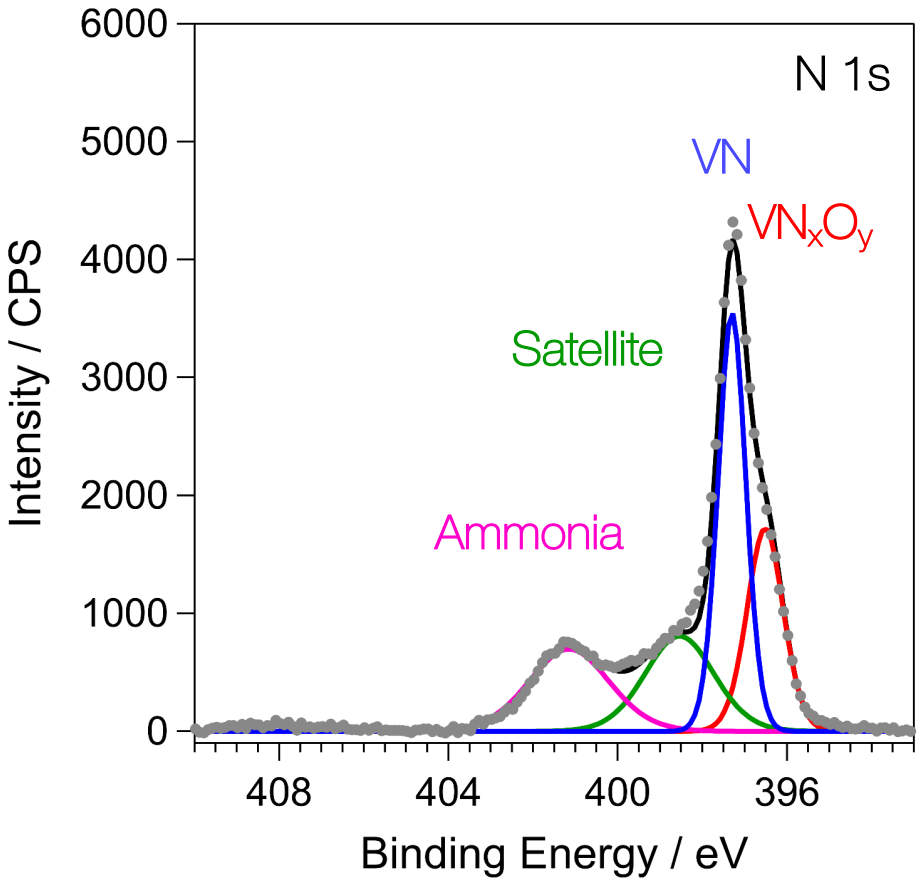
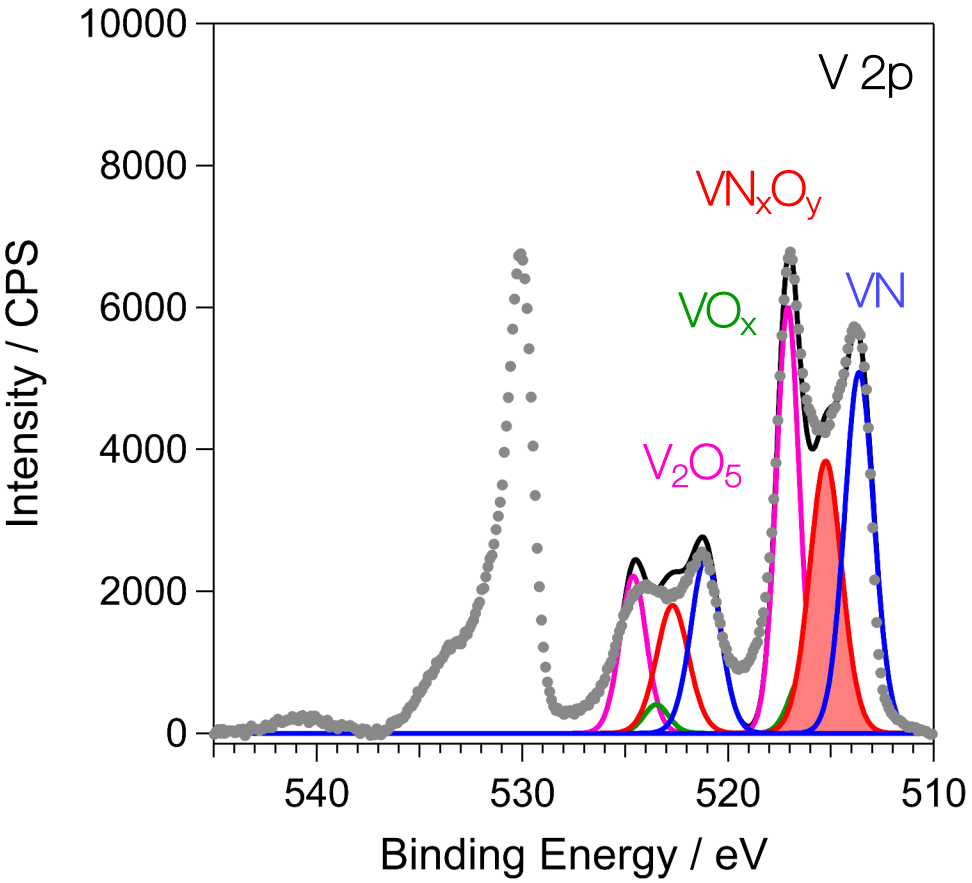
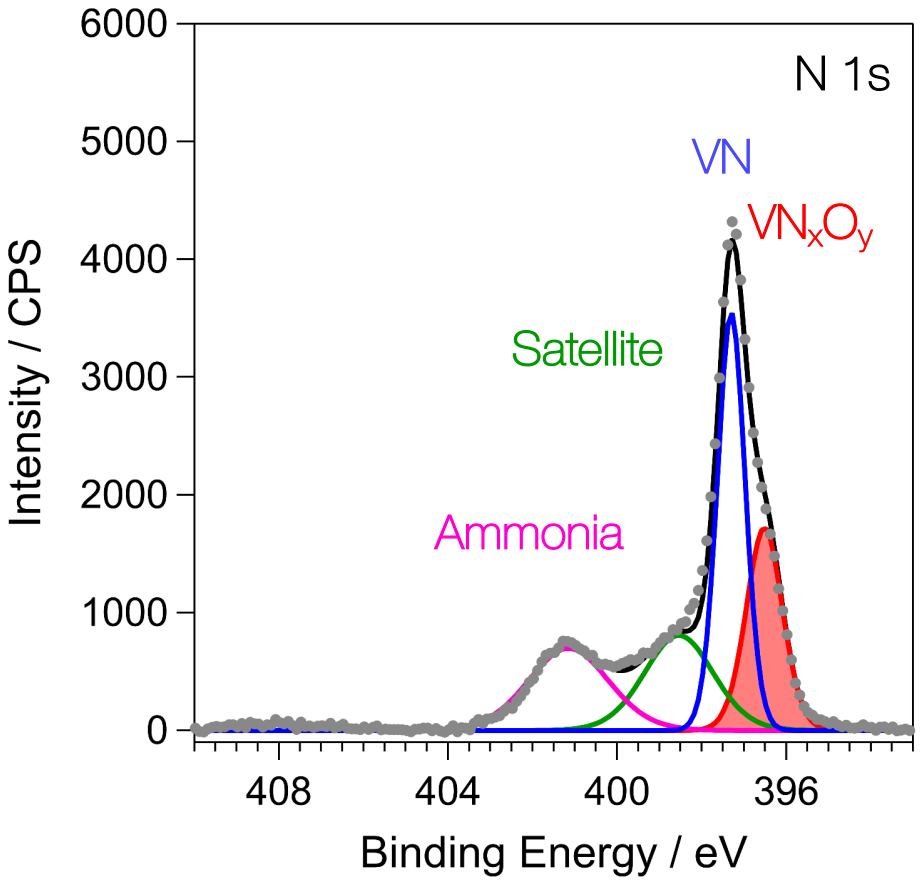




XPS of VN Catalysts before ENRR





Based on the ratio of V 2p and N 1s bands assigned to VN_xO_y, and assuming a +3 oxidation state of V, the composition of the oxynitride is $VN_{0.7}O_{0.45}$

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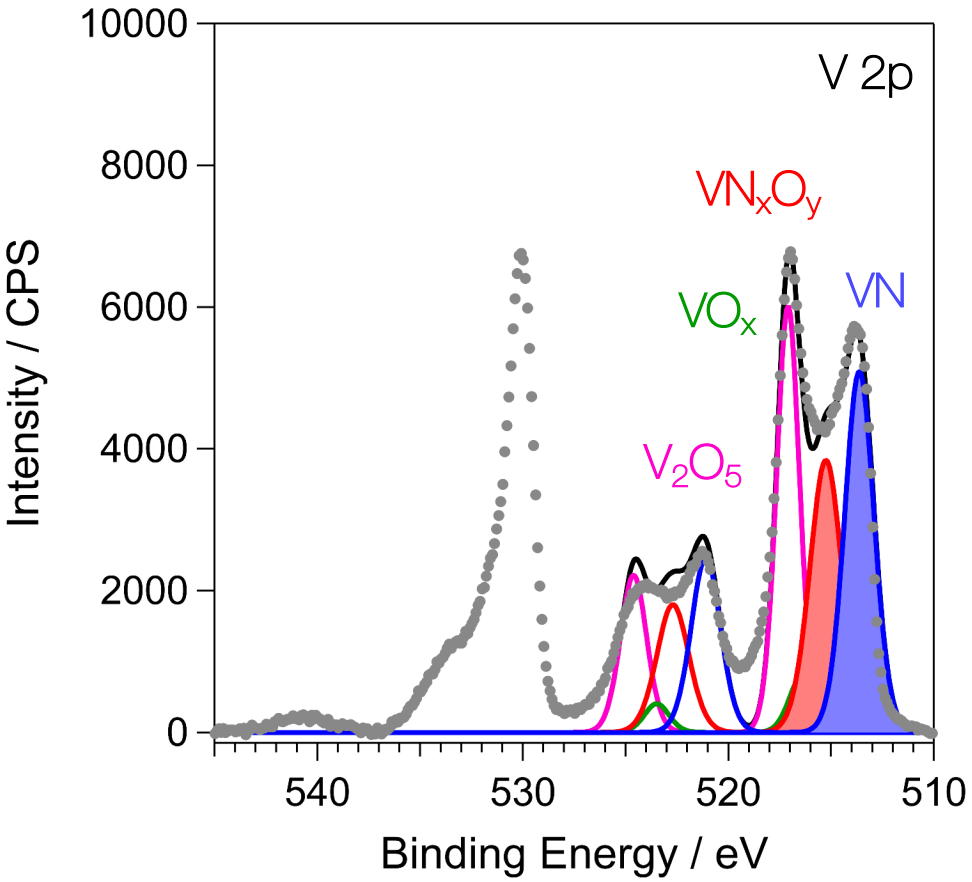
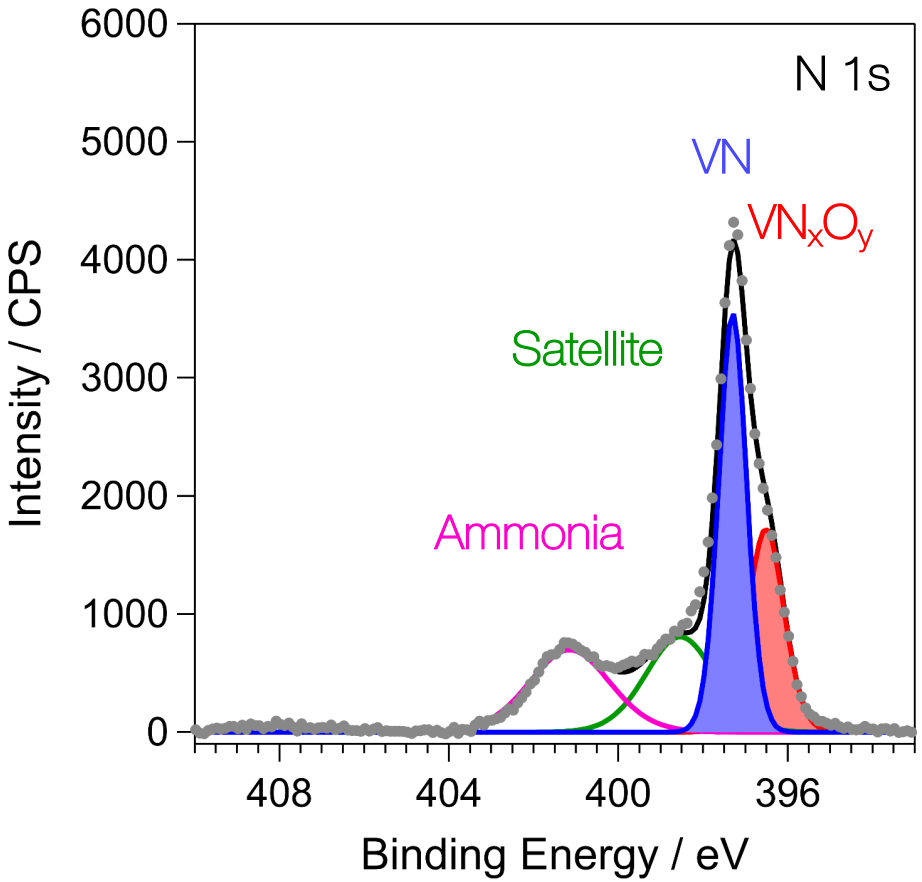
XPS of VN Catalysts before ENRR

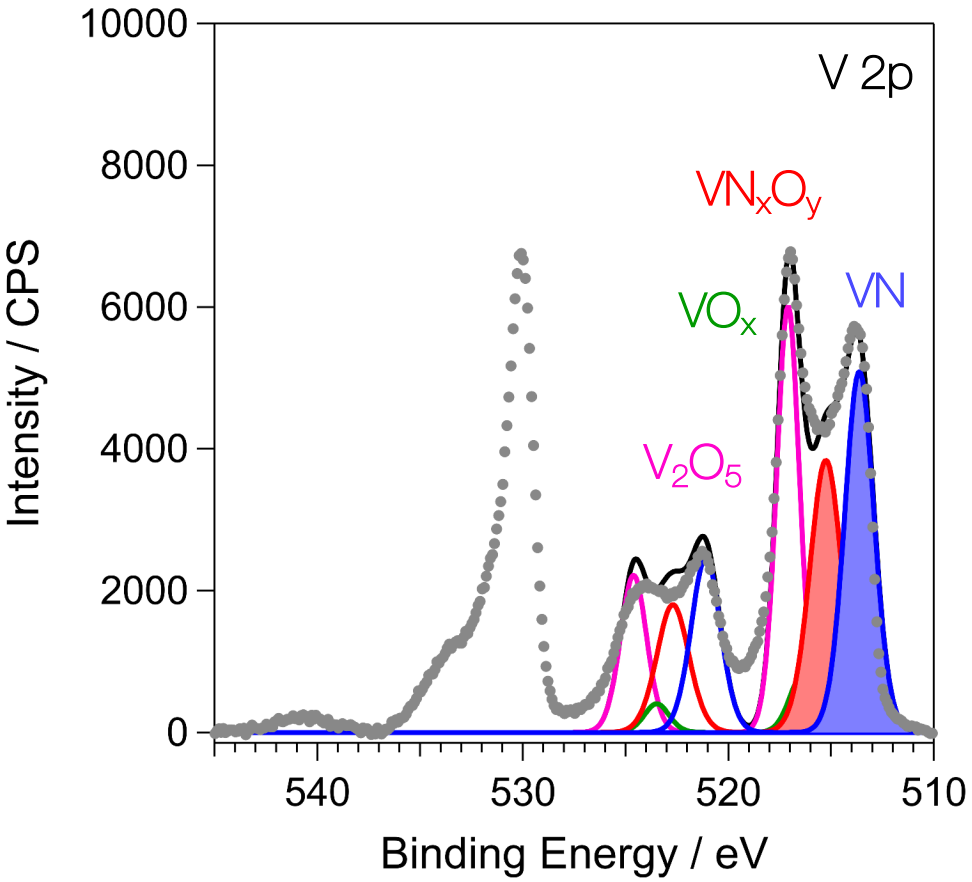


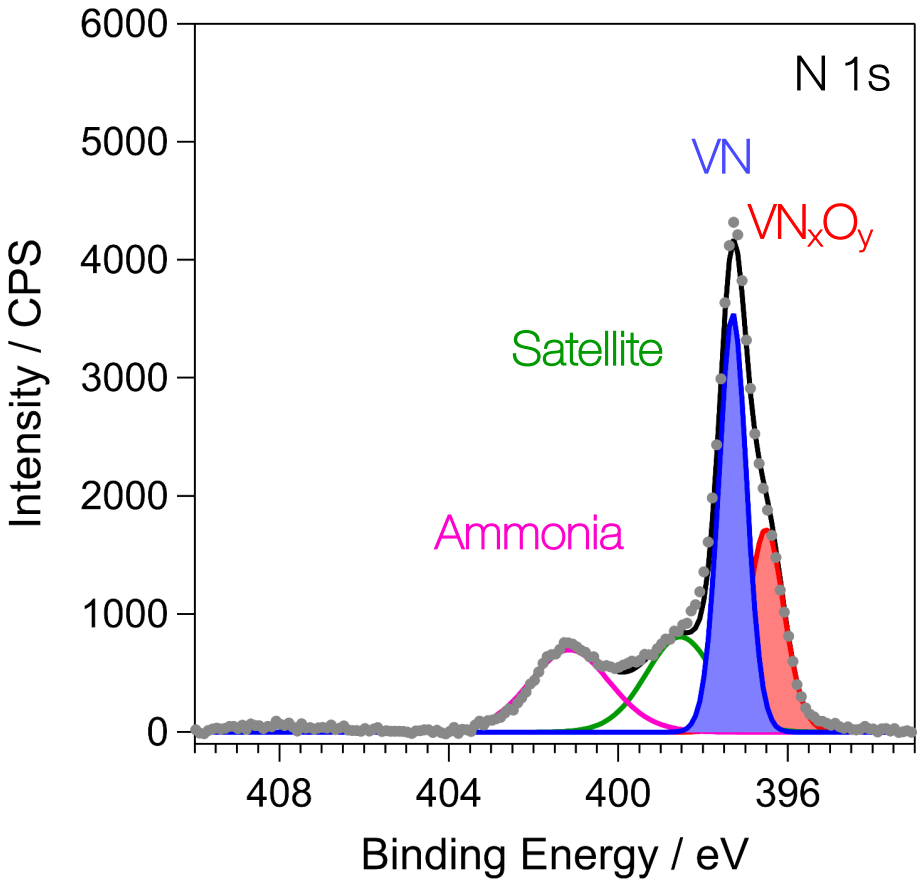


$VN_{0.7}O_{0.45}$: VN ratio on the fresh VN is ~0.91

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

XPS of VN Catalysts before ENRR



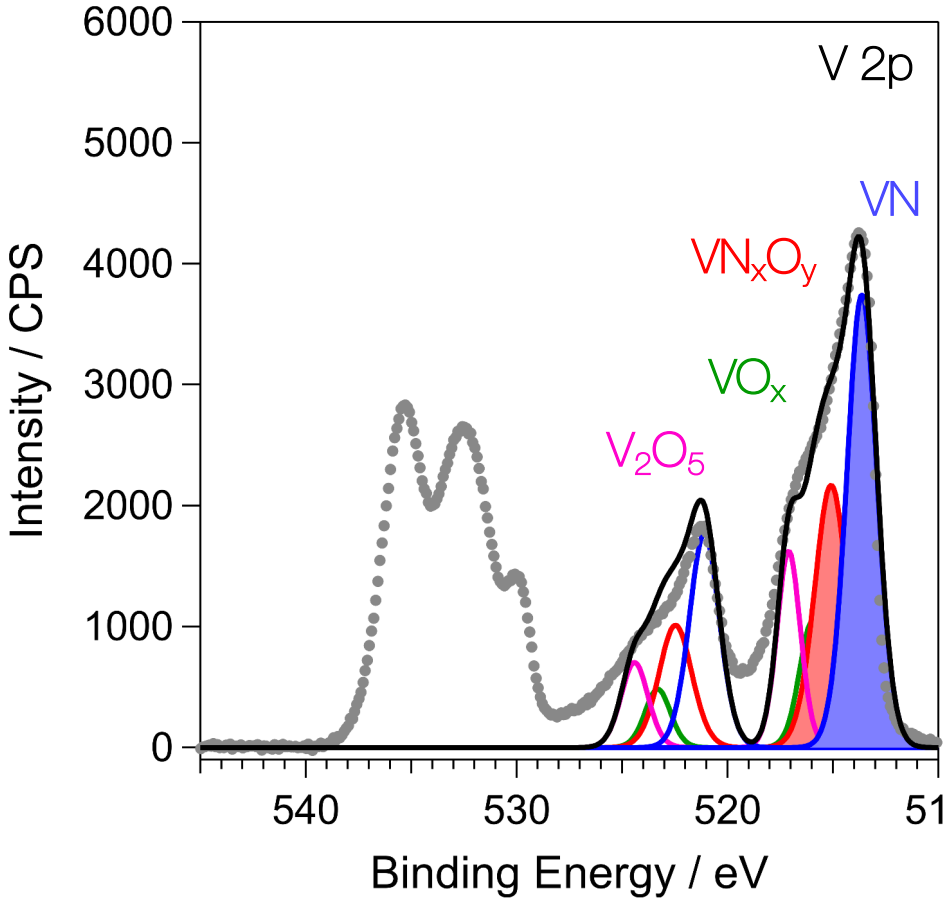


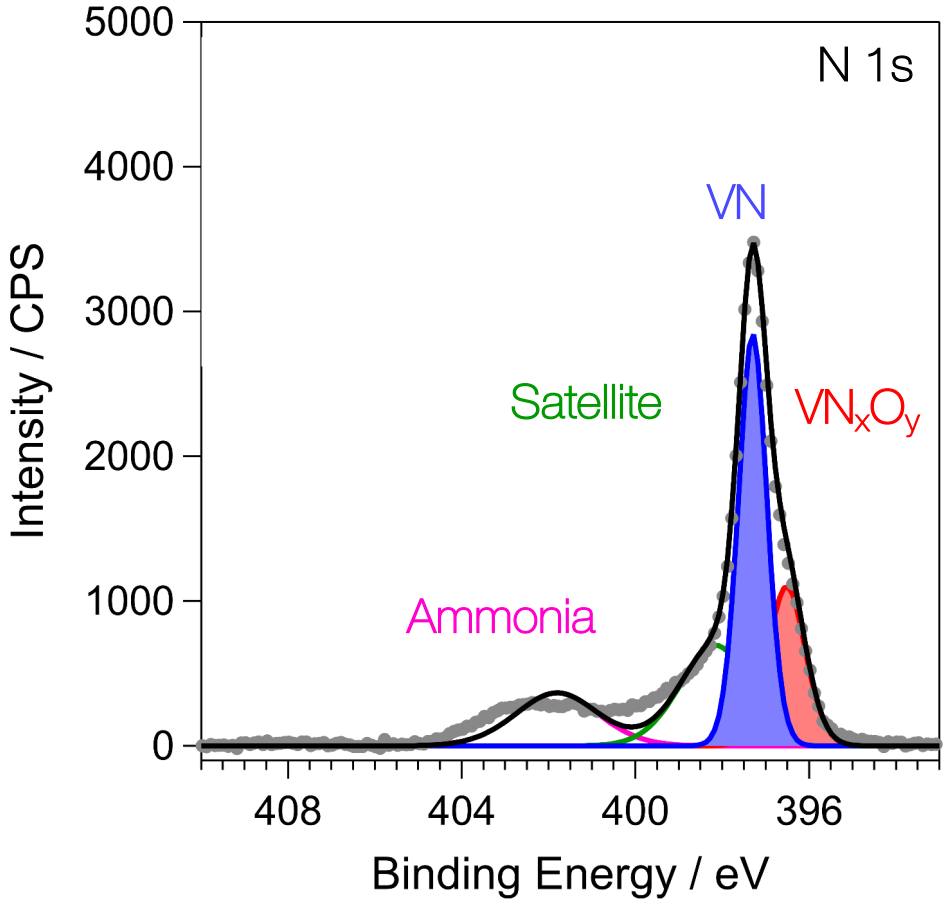
$VN_{0.7}O_{0.45}$: VN ratio on the fresh VN is ~0.91

How does the surface composition change during ENRR?

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

XPS of VN Catalysts after ENRR





$VN_{0.7}O_{0.45}$: VN ratio decreases to 0.77 after ENRR at −0.1 V for 1 h

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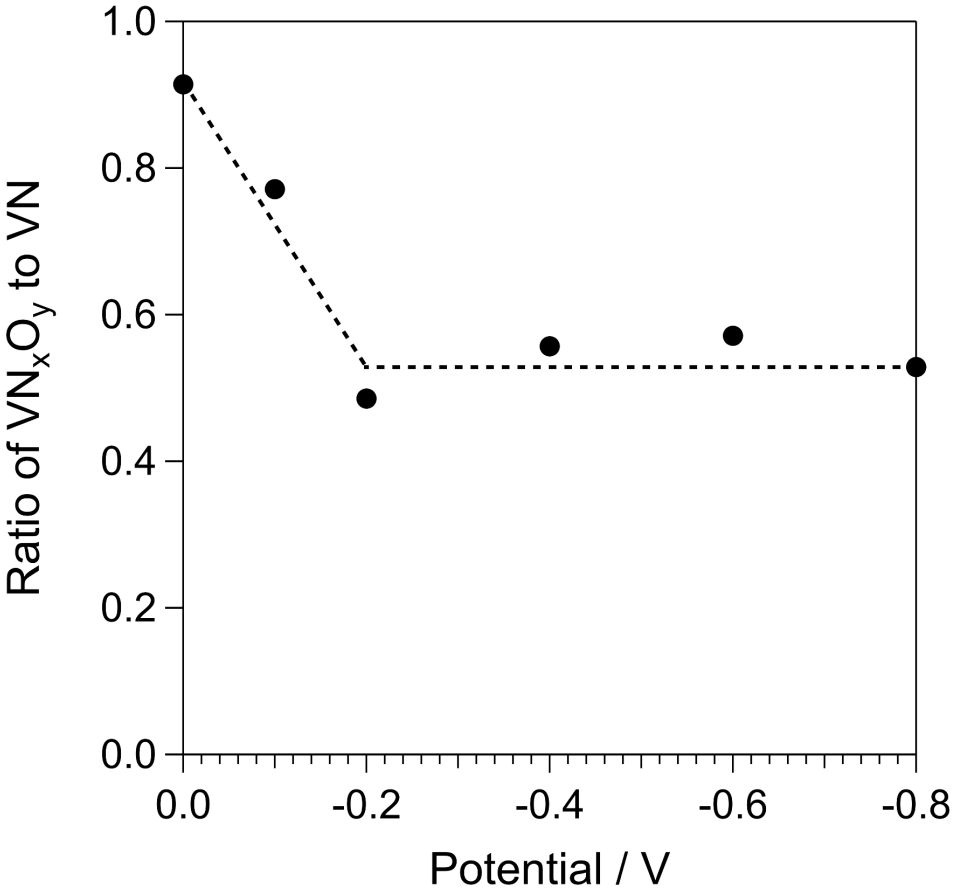
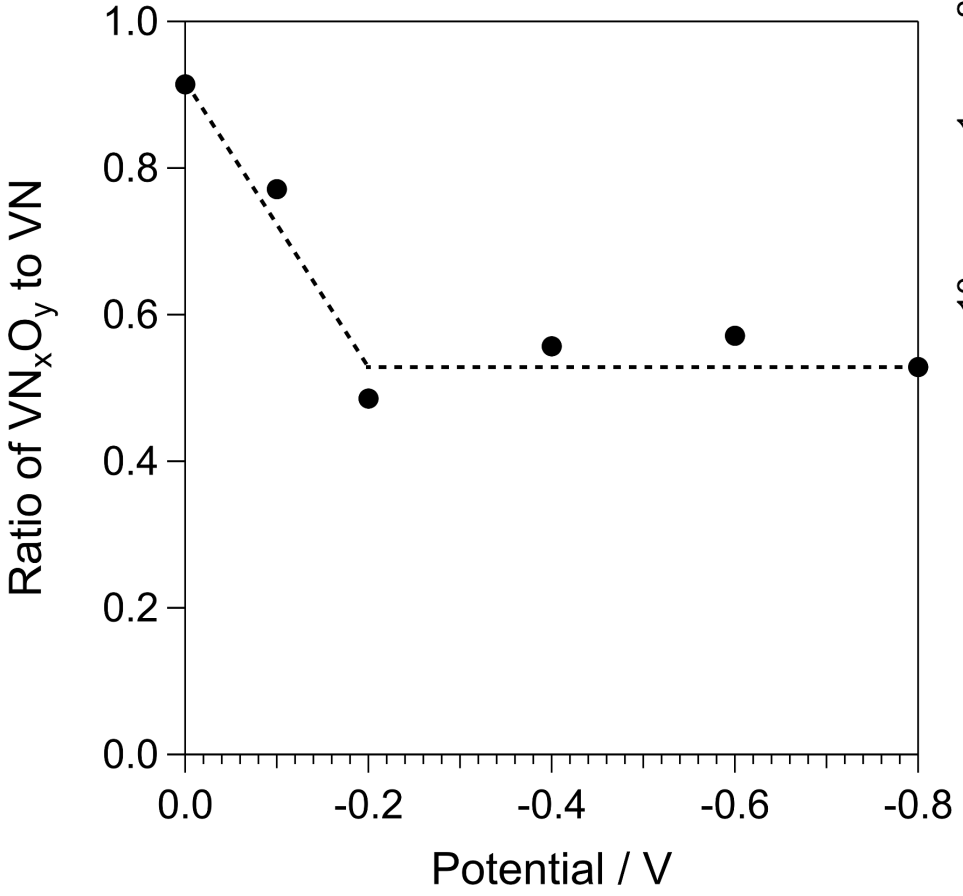
XPS of VN Catalysts after ENRR

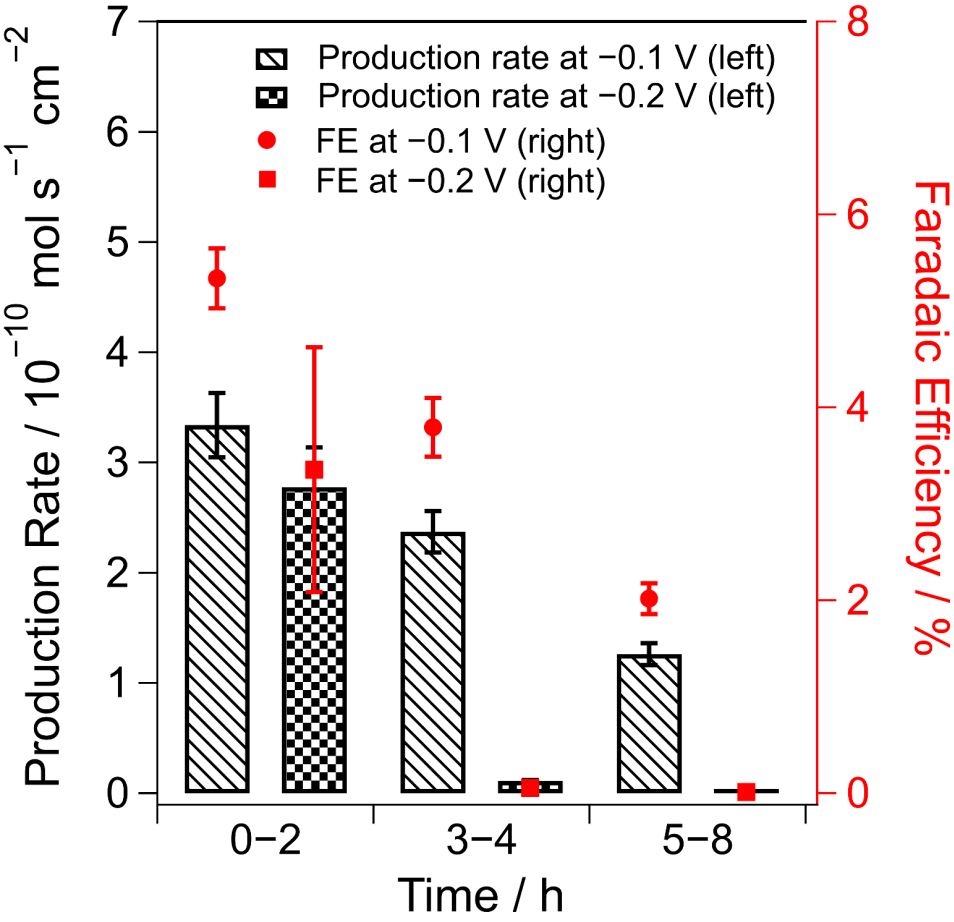


$VN_{0.7}O_{0.45}$: VN ratio stabilizes at 0.54 after ENRR for 1 h at < -0.2 V

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

XPS of VN Catalysts after ENRR





$VN_{0.7}O_{0.45}$: VN ratio stabilizes at 0.54 after ENRR for 1 h at < -0.2 V

Almost no ammonia is produced after ENRR for 1 h at < -0.2 V

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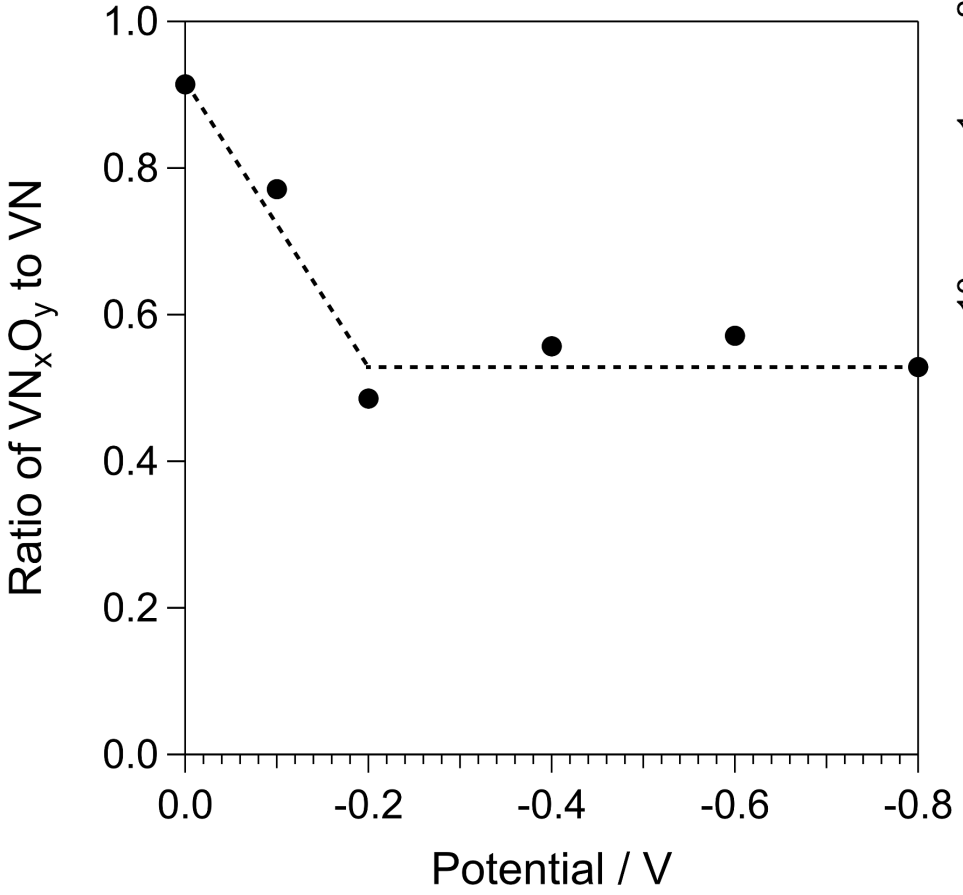
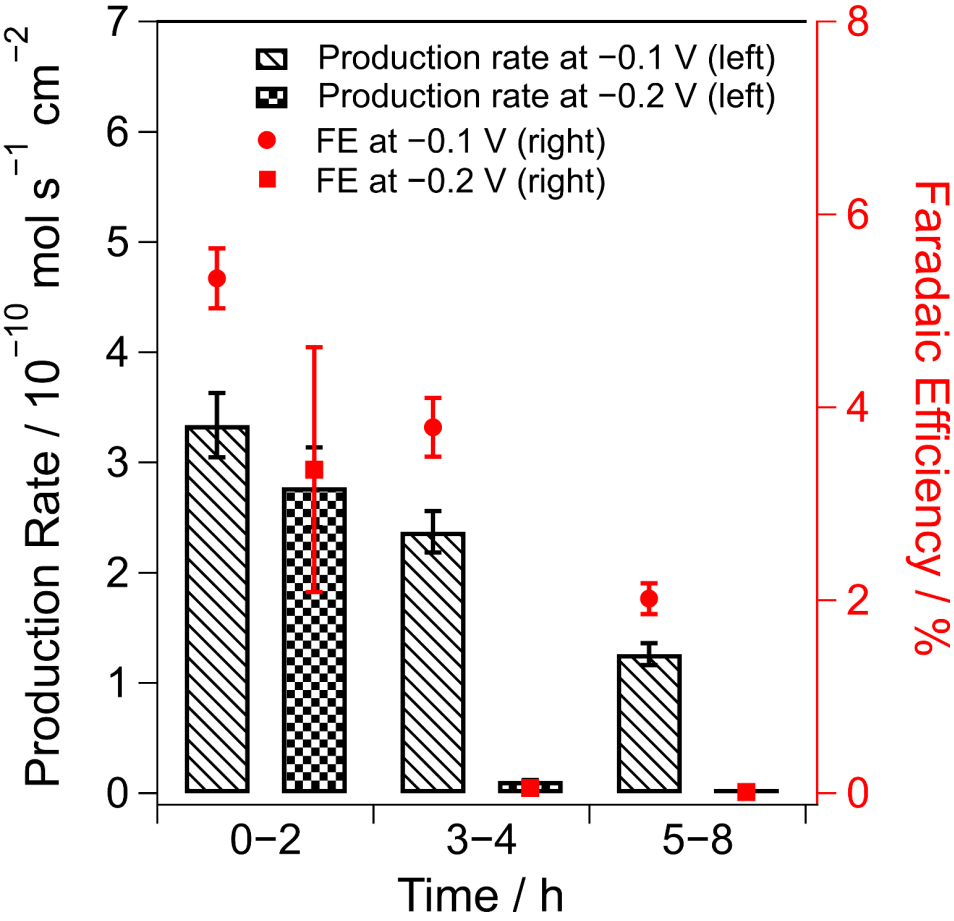
XPS of VN Catalysts after ENRR





$VN_{0.7}O_{0.45}$ is likely the active phase for ENRR

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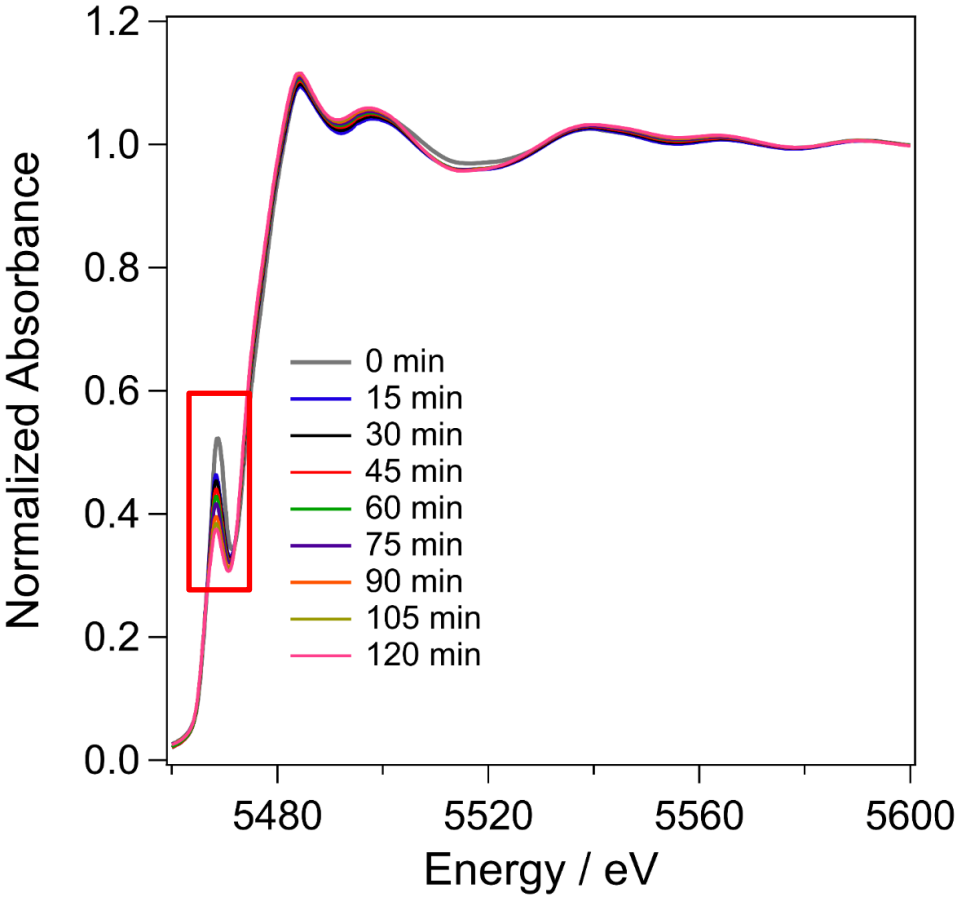
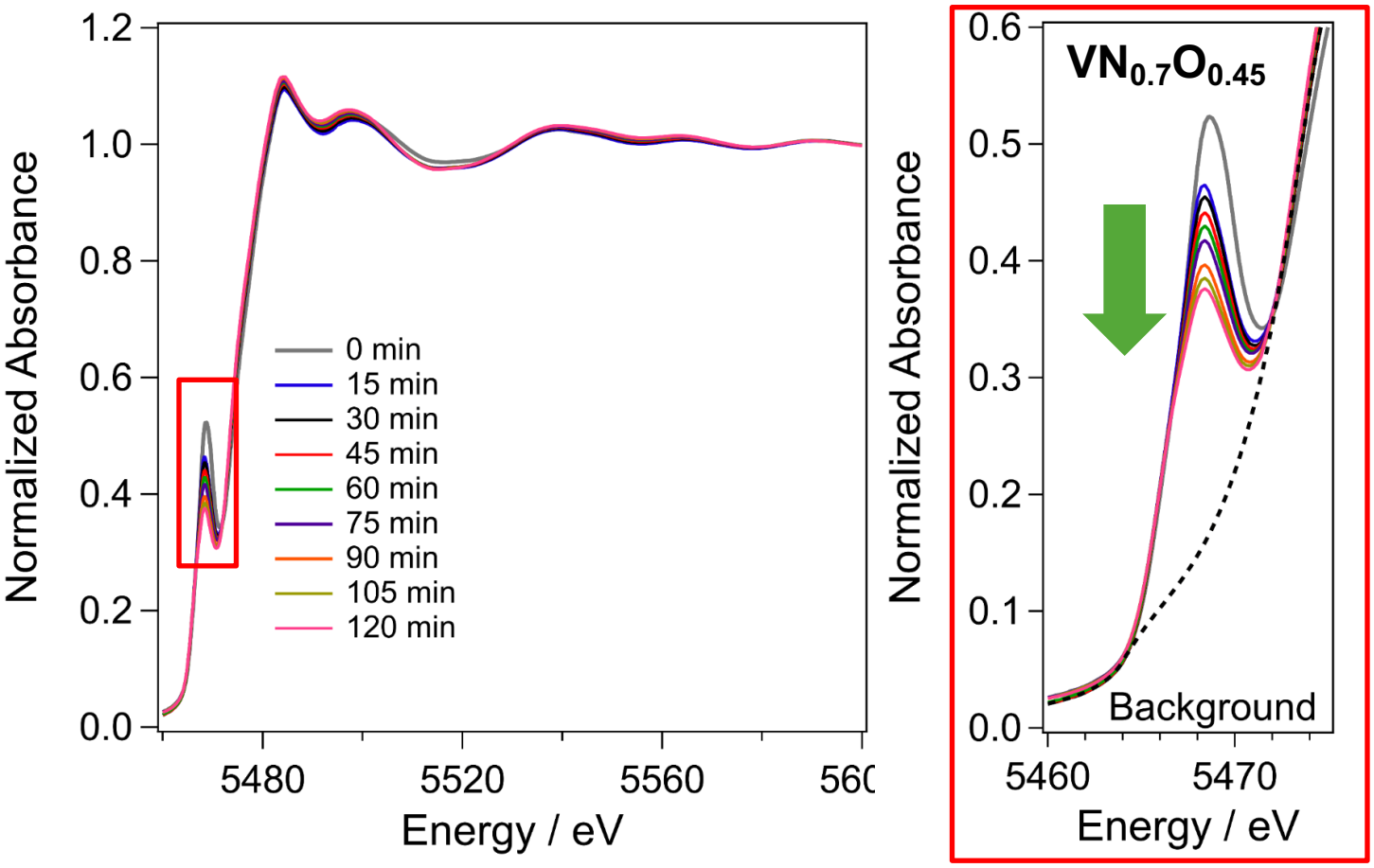
Operando XAS of VN during ENRR



The Pre-edge peak confirms the existence of $VN_{0.7}O_{0.45}$ on the surface of VN

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

Operando XAS of VN during ENRR



The Pre-edge peak confirms the existence of $VN_{0.7}O_{0.45}$ on the surface of VN

$VN_{0.7}O_{0.45}$ is consumed during ENRR at -0.1 V

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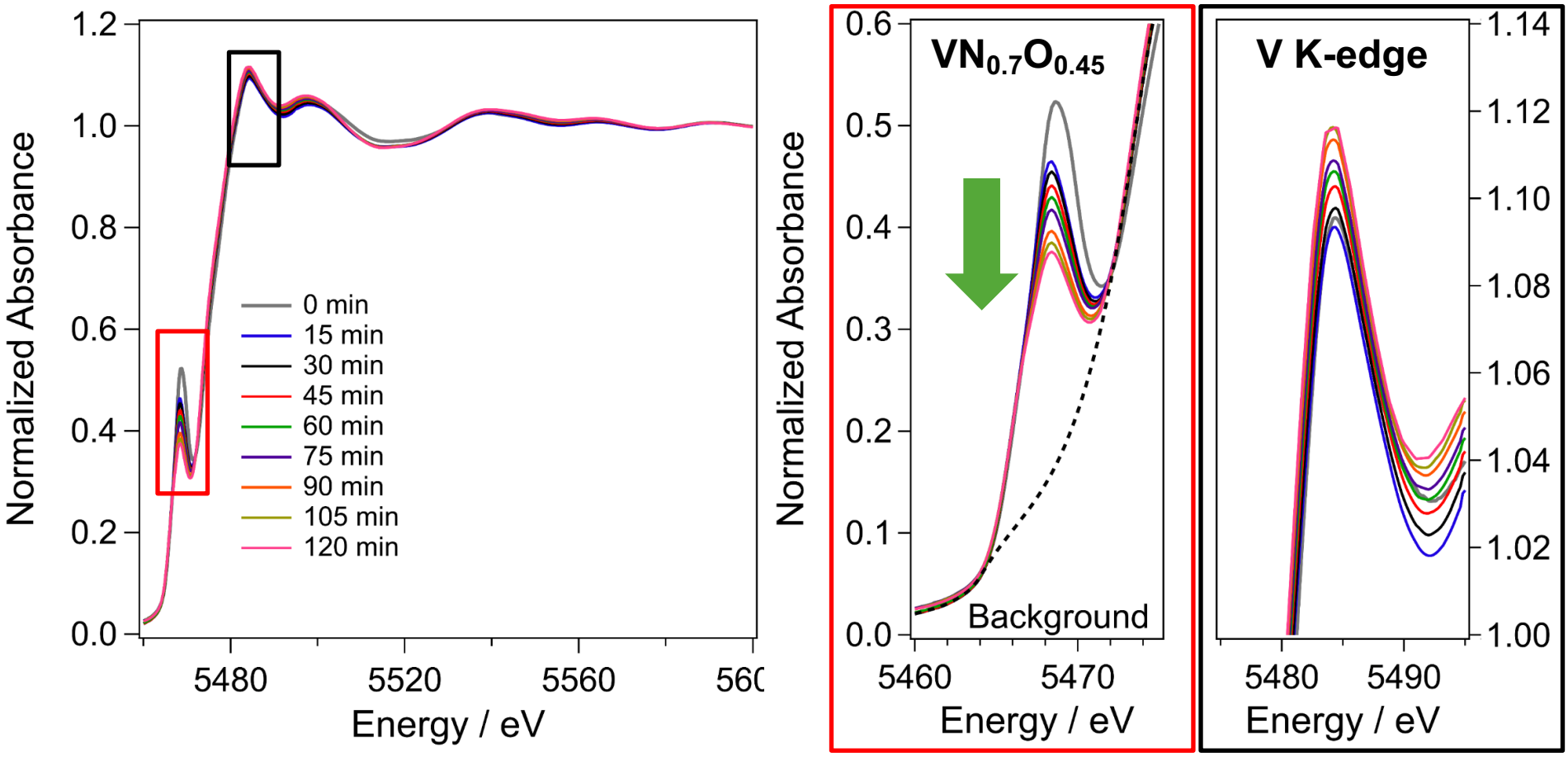
Operando XAS of VN during ENRR



The K-edge peak randomly changes with time and is relatively stable

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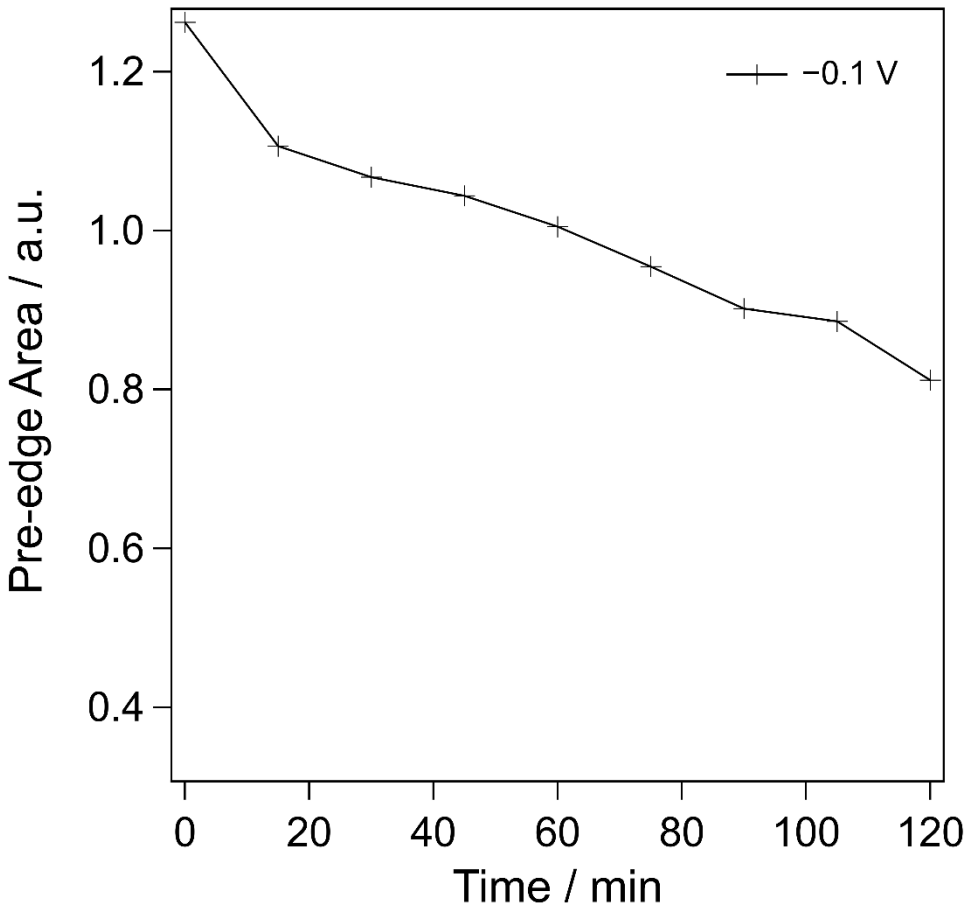
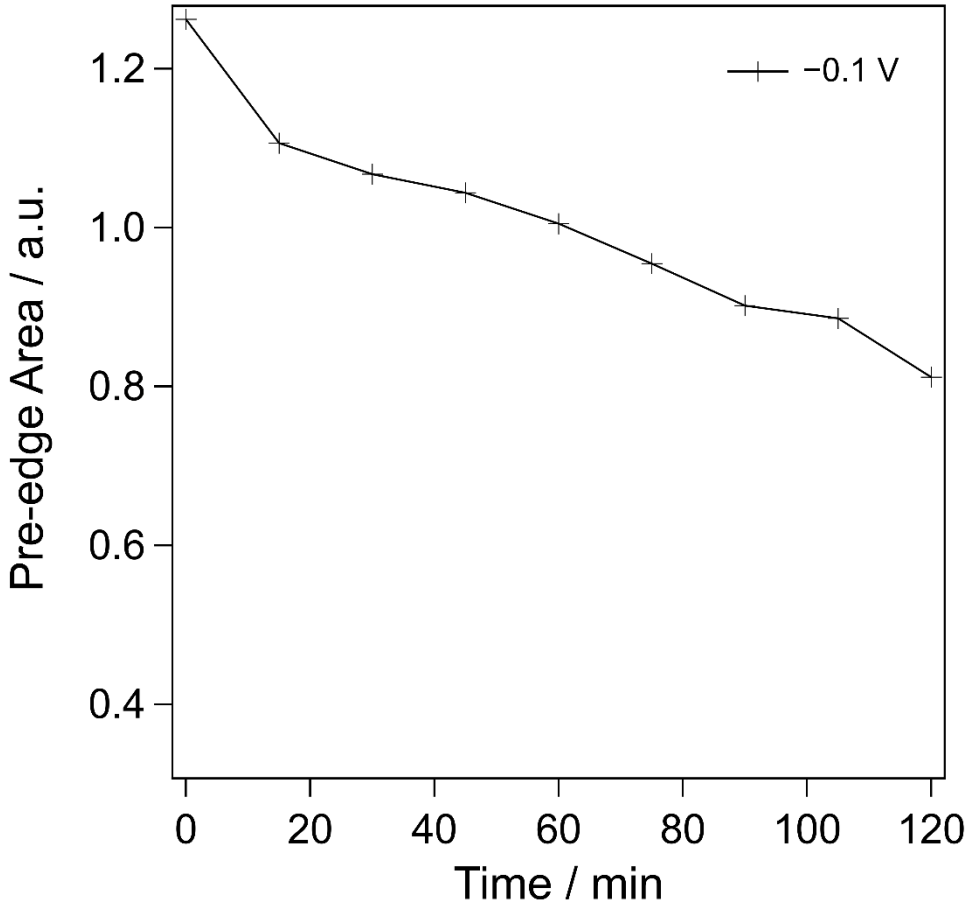
Operando XAS of VN during ENRR

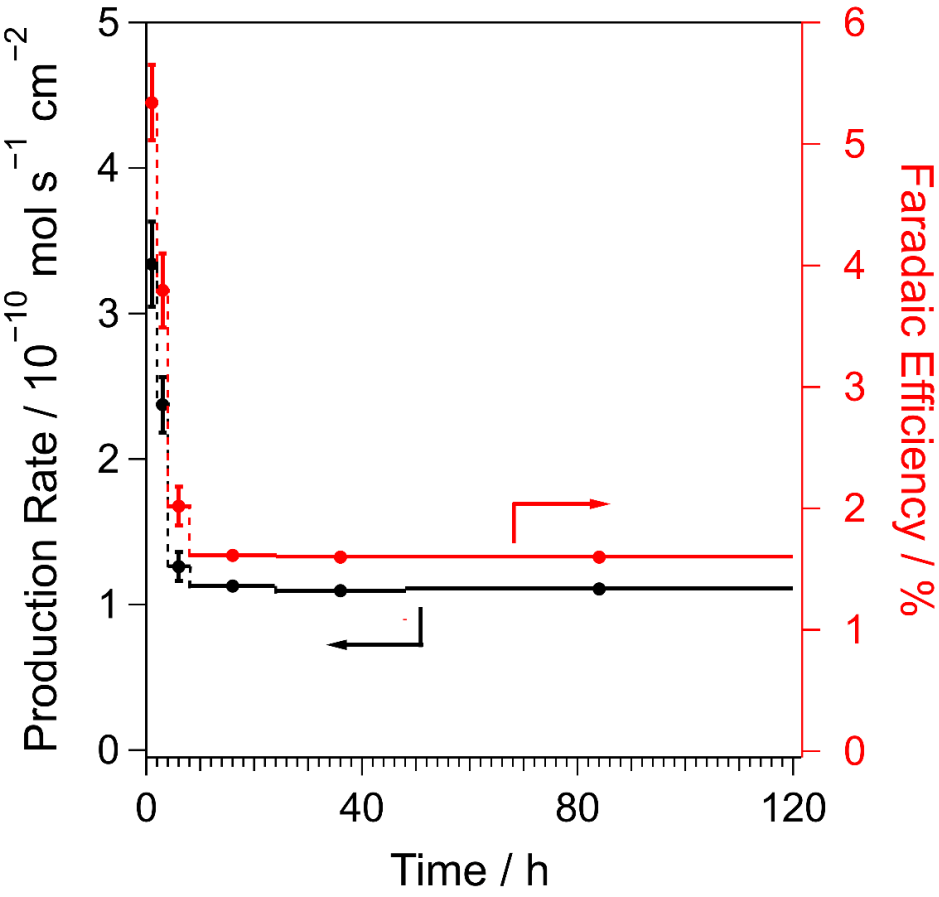


- **$VN_{0.7}O_{0.45}$ is consumed during ENRR**

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

Operando XAS of VN during ENRR





- **$VN_{0.7}O_{0.45}$ is consumed during ENRR**
- **The catalysts deactivate during the first 4 h**

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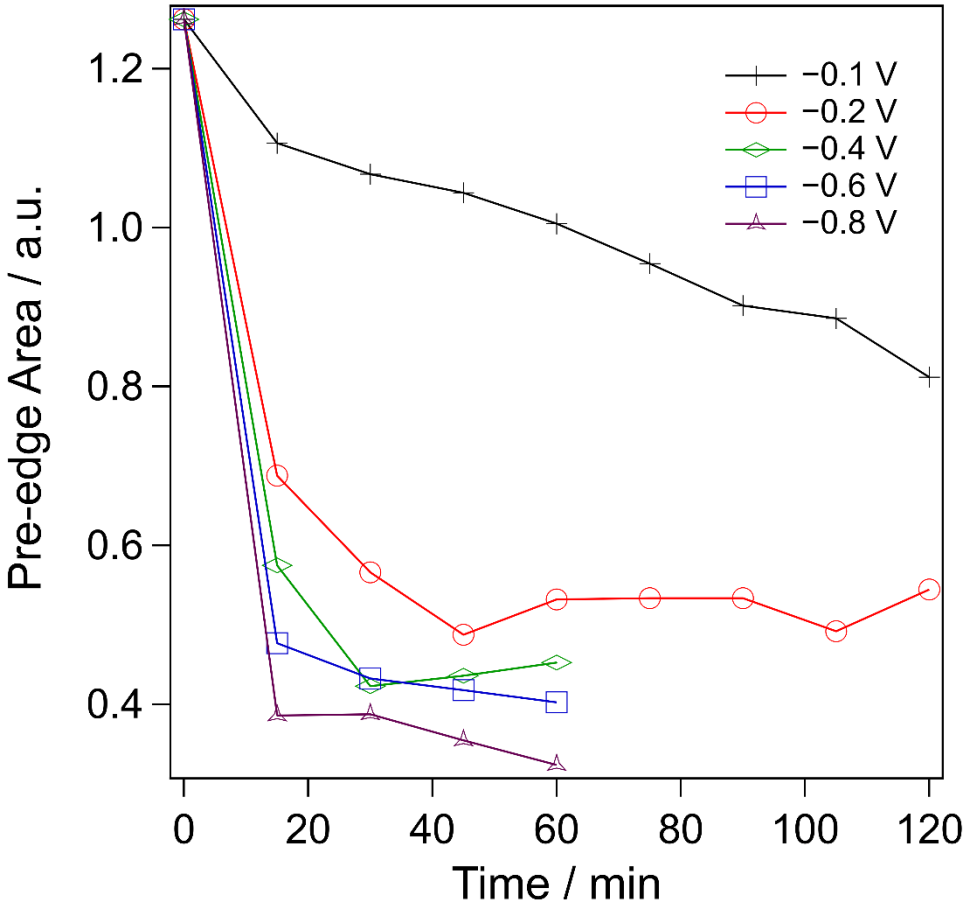
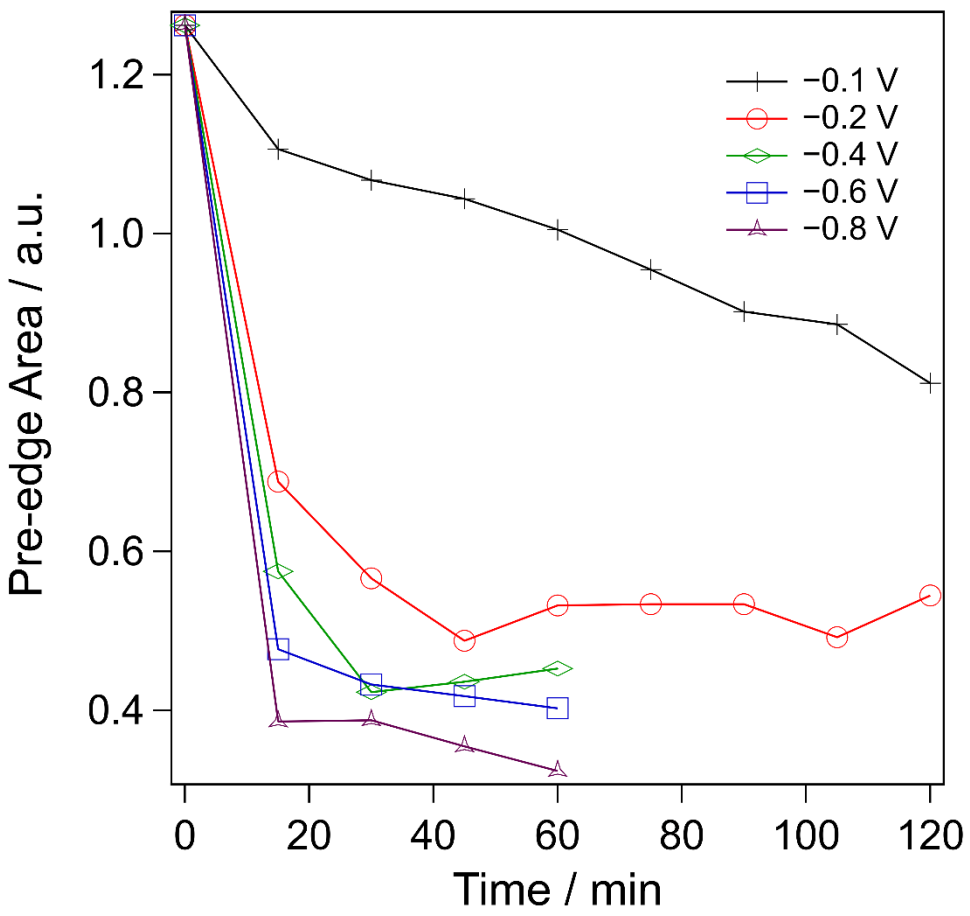
Operando XAS of VN during ENRR

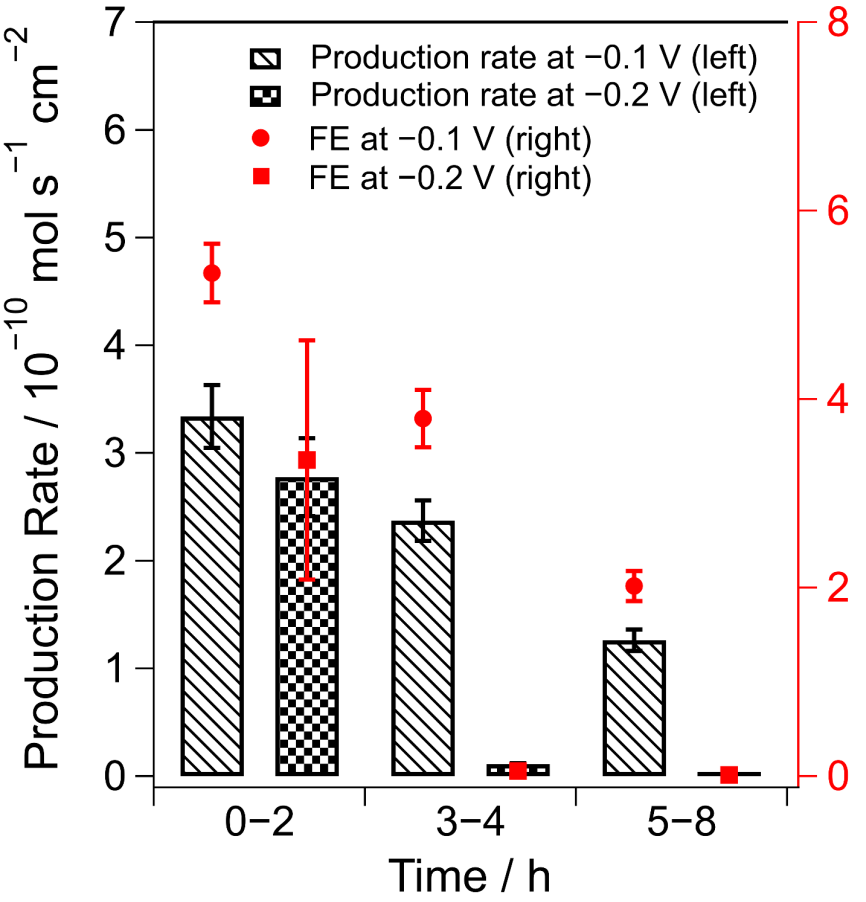


- **The consumption rate of $VN_{0.7}O_{0.45}$ is slower at -0.1 V**
- **Similar and stable amount of $VN_{0.7}O_{0.45}$ is reached within 1h at potentials < -0.2 V**

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

Operando XAS of VN during ENRR





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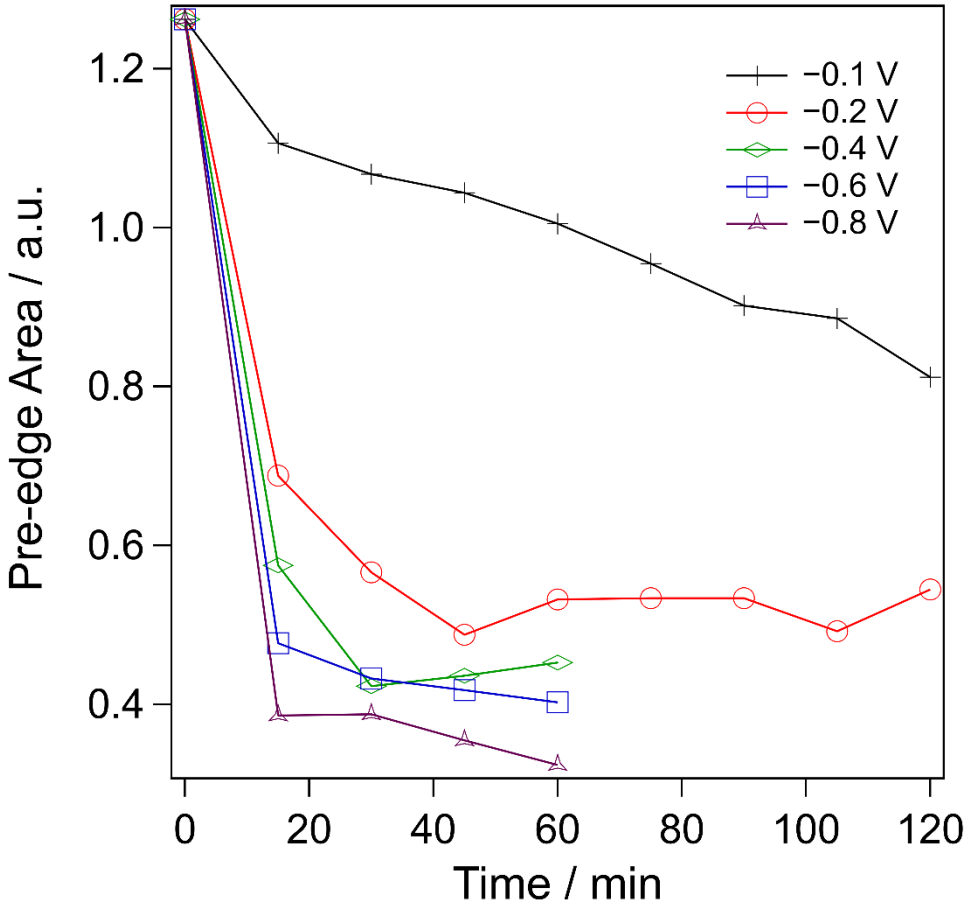
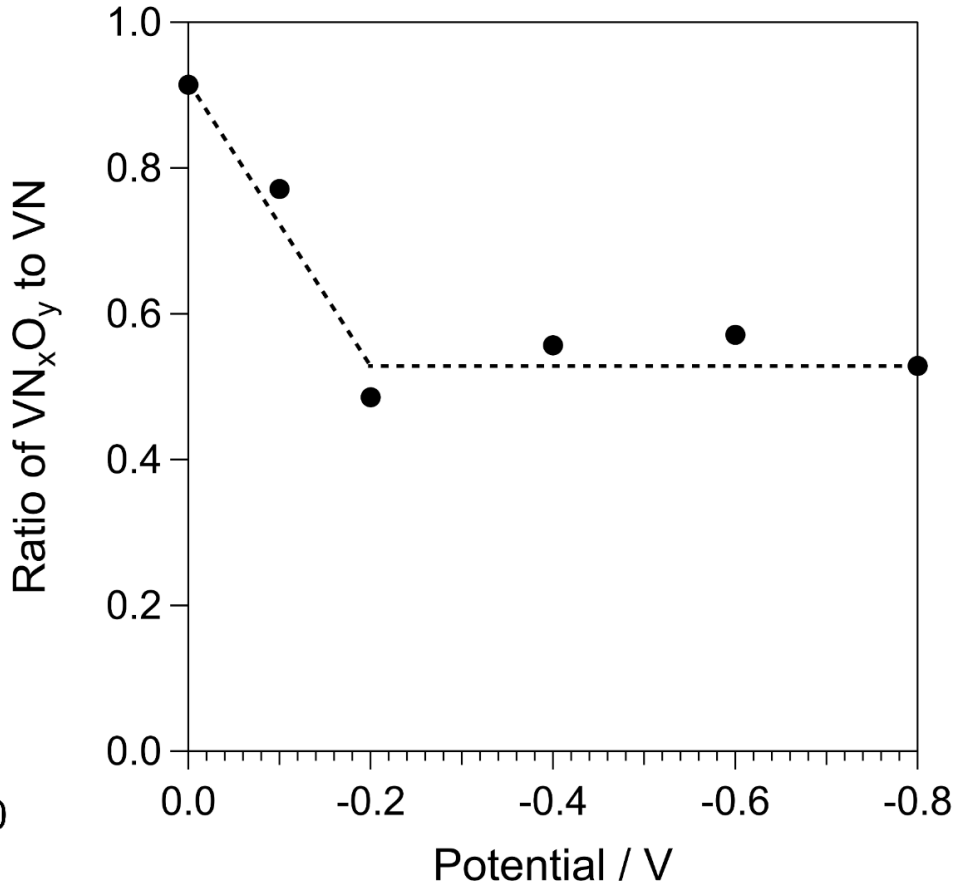
Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

Operando XAS of VN during ENRR

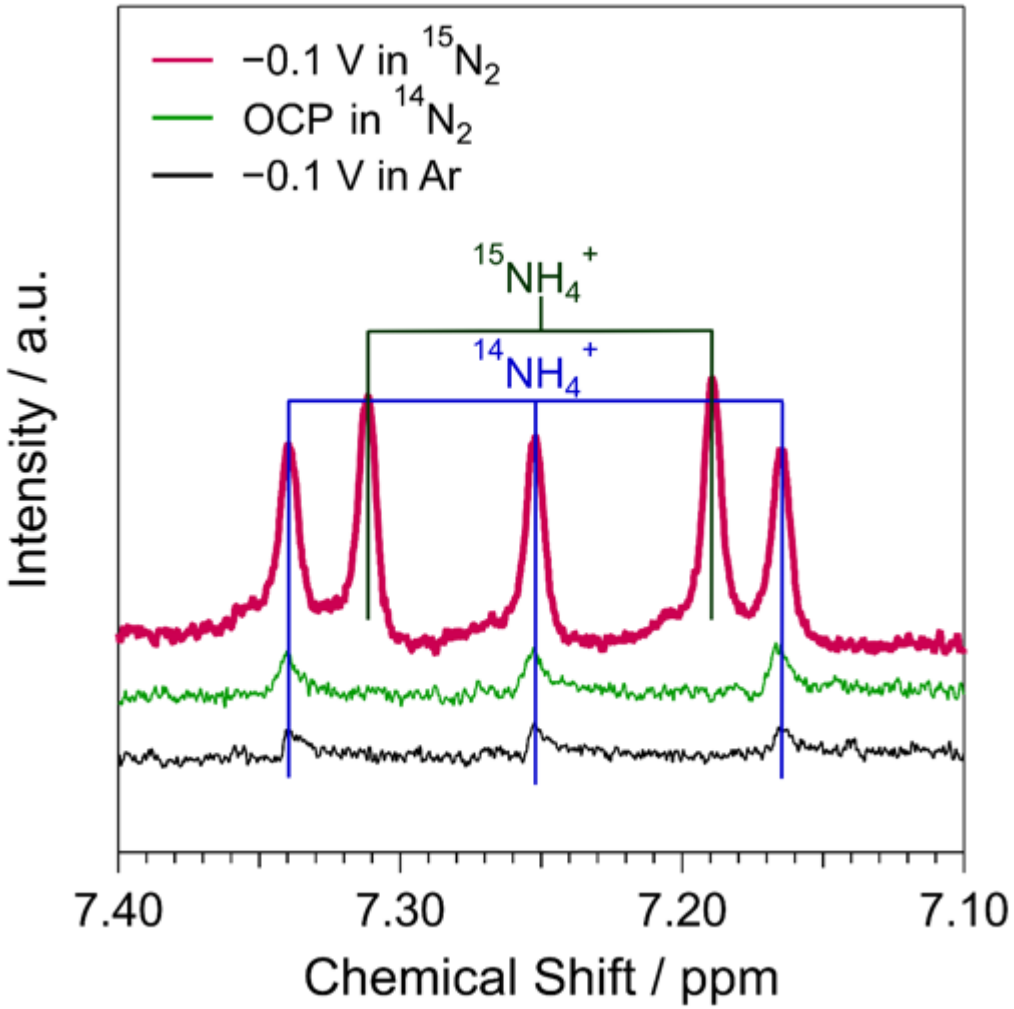




$VN_{0.7}O_{0.45}$ is the active phase for ENRR

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

ENRR Occurs via the Mars-van Krevelen Mechanism



1. Confirms N_2 activation on VN

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

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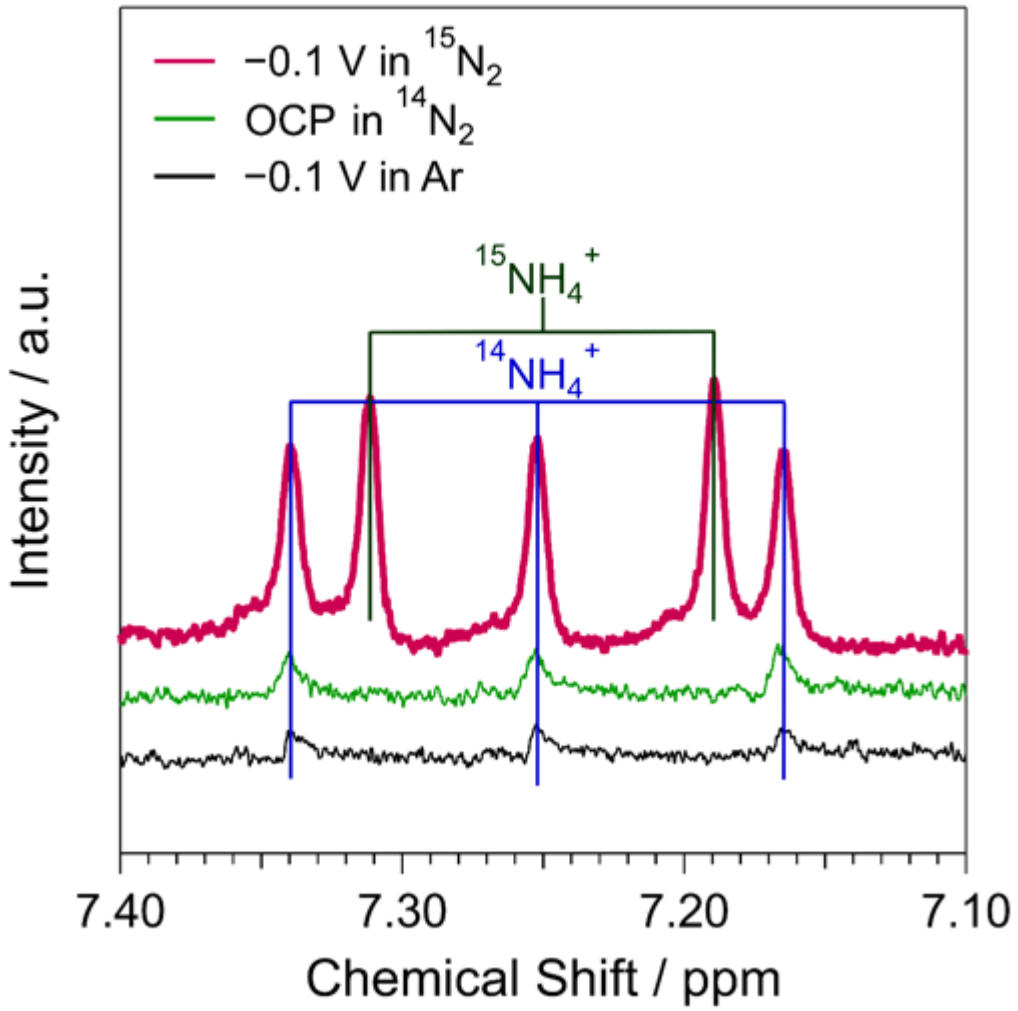

1. Confirms N_2 activation on VN

2. Surface N participates in ENRR

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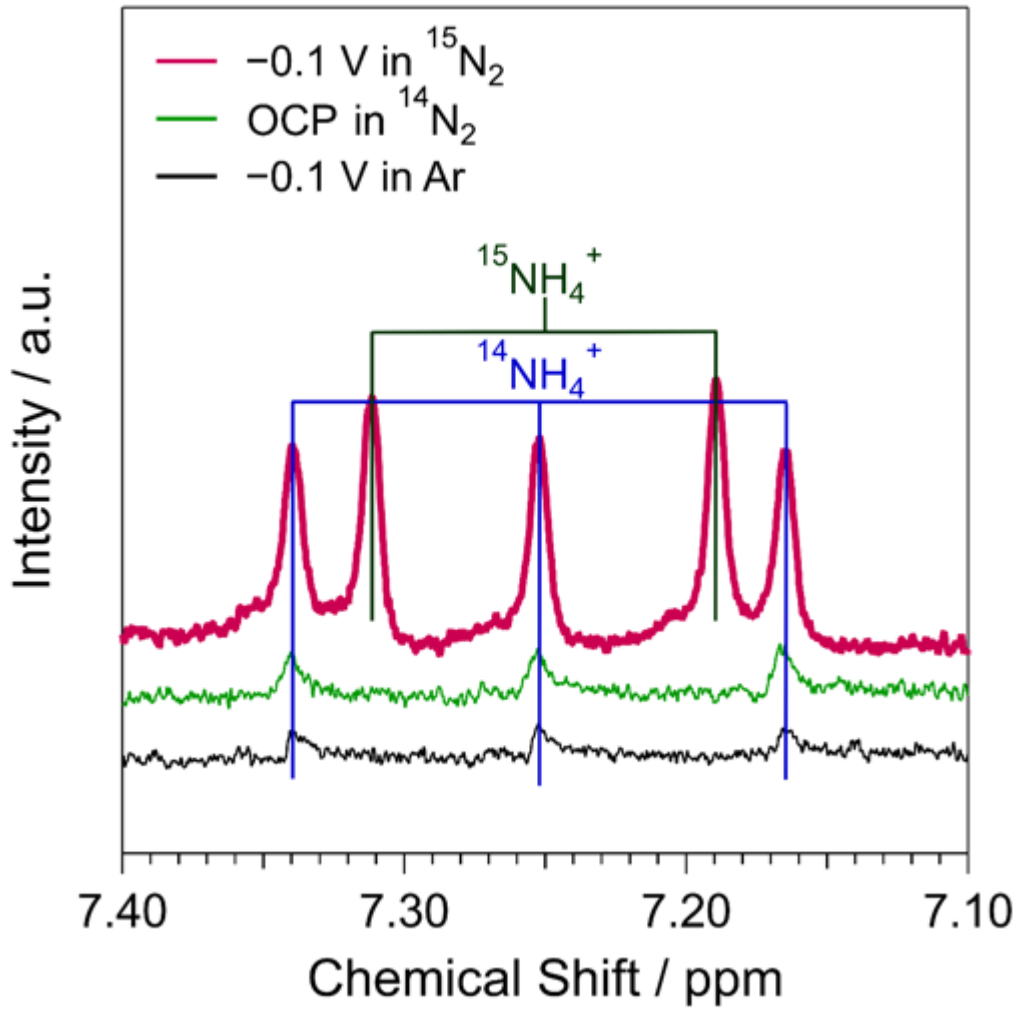

1. Confirms N_2 activation on VN

2. Surface N participates in ENRR

3. ENRR follows MvK mechanism

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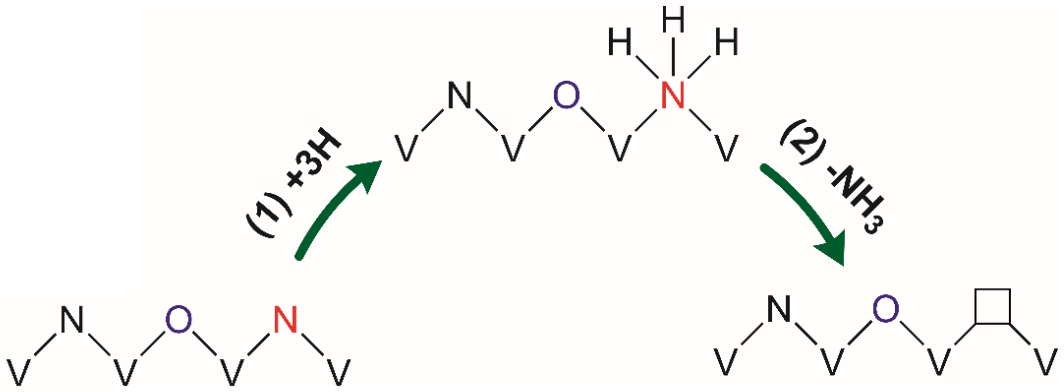

Nitrogen Reduction

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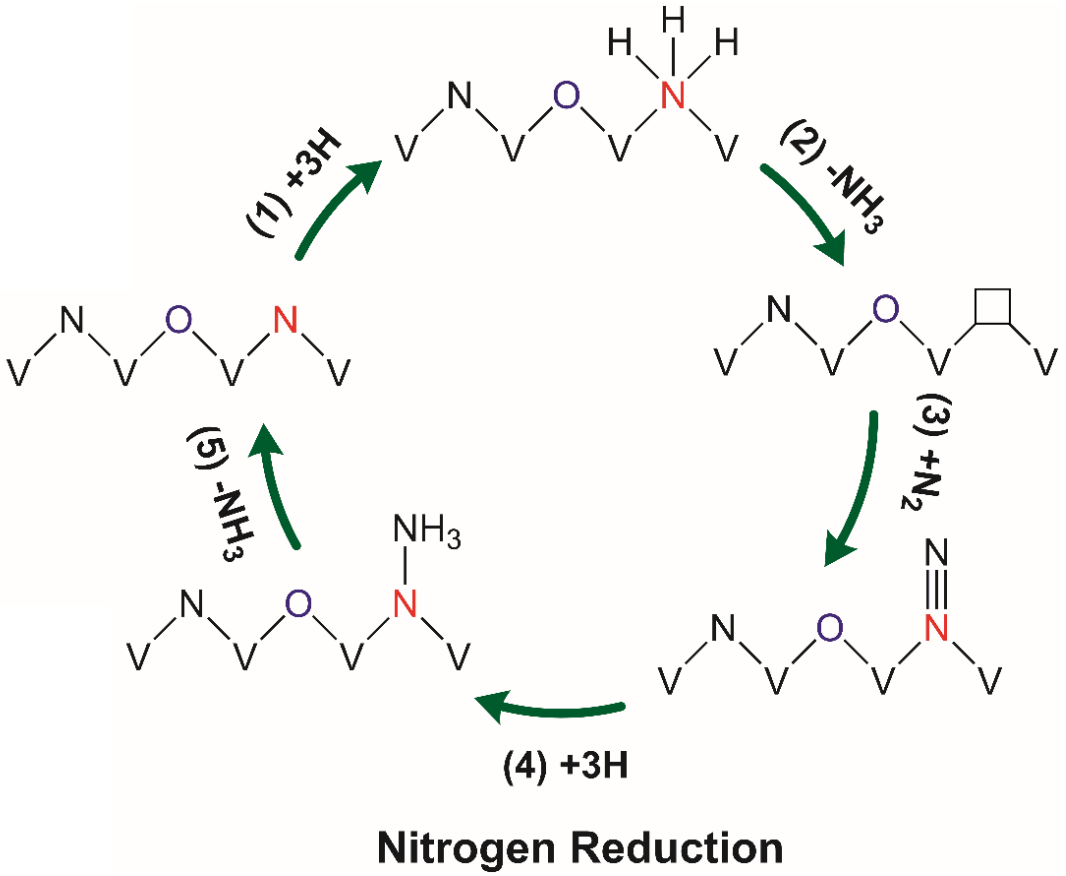
ENRR Occurs via the Mars-van Krevelen Mechanism



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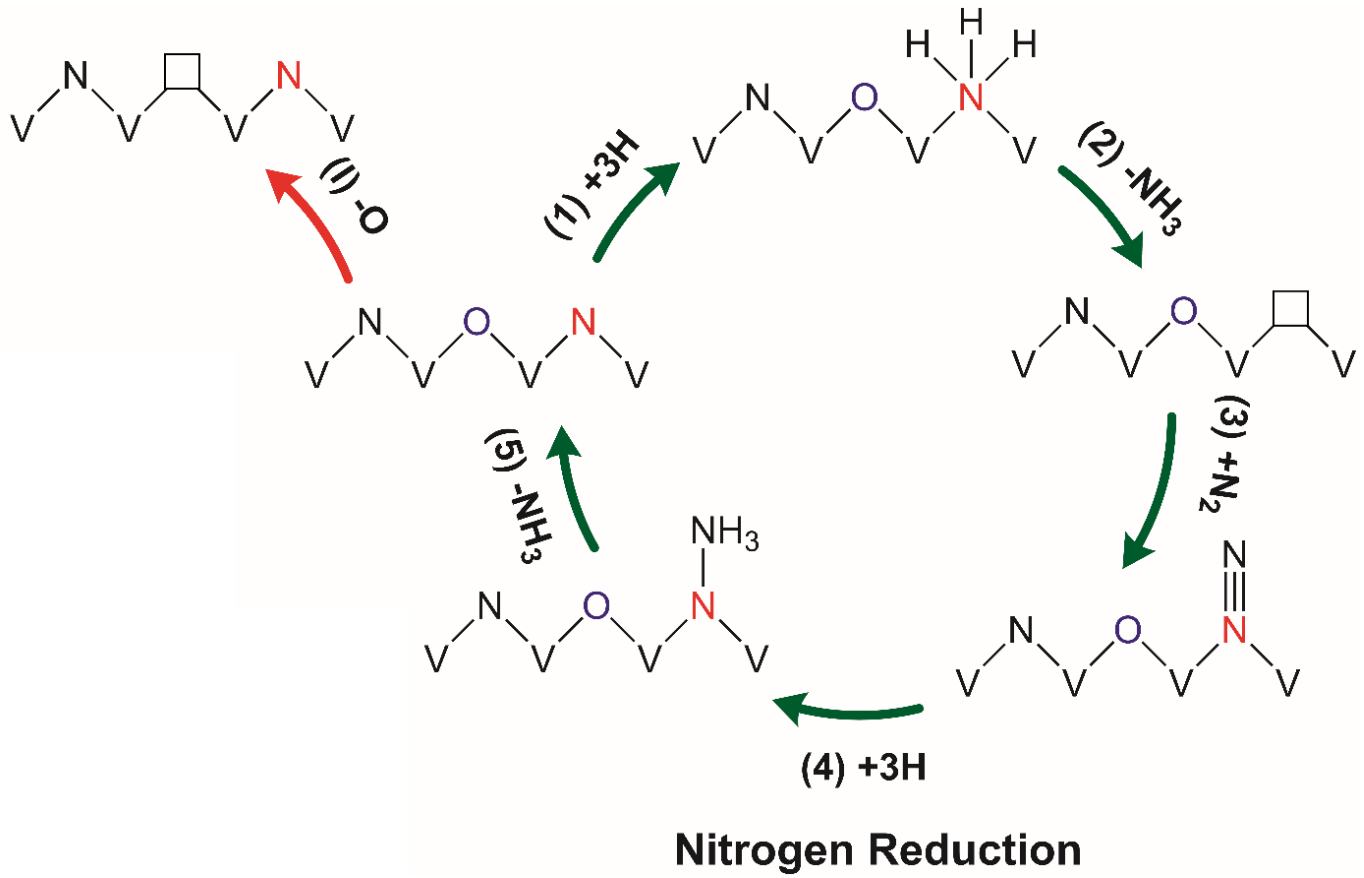

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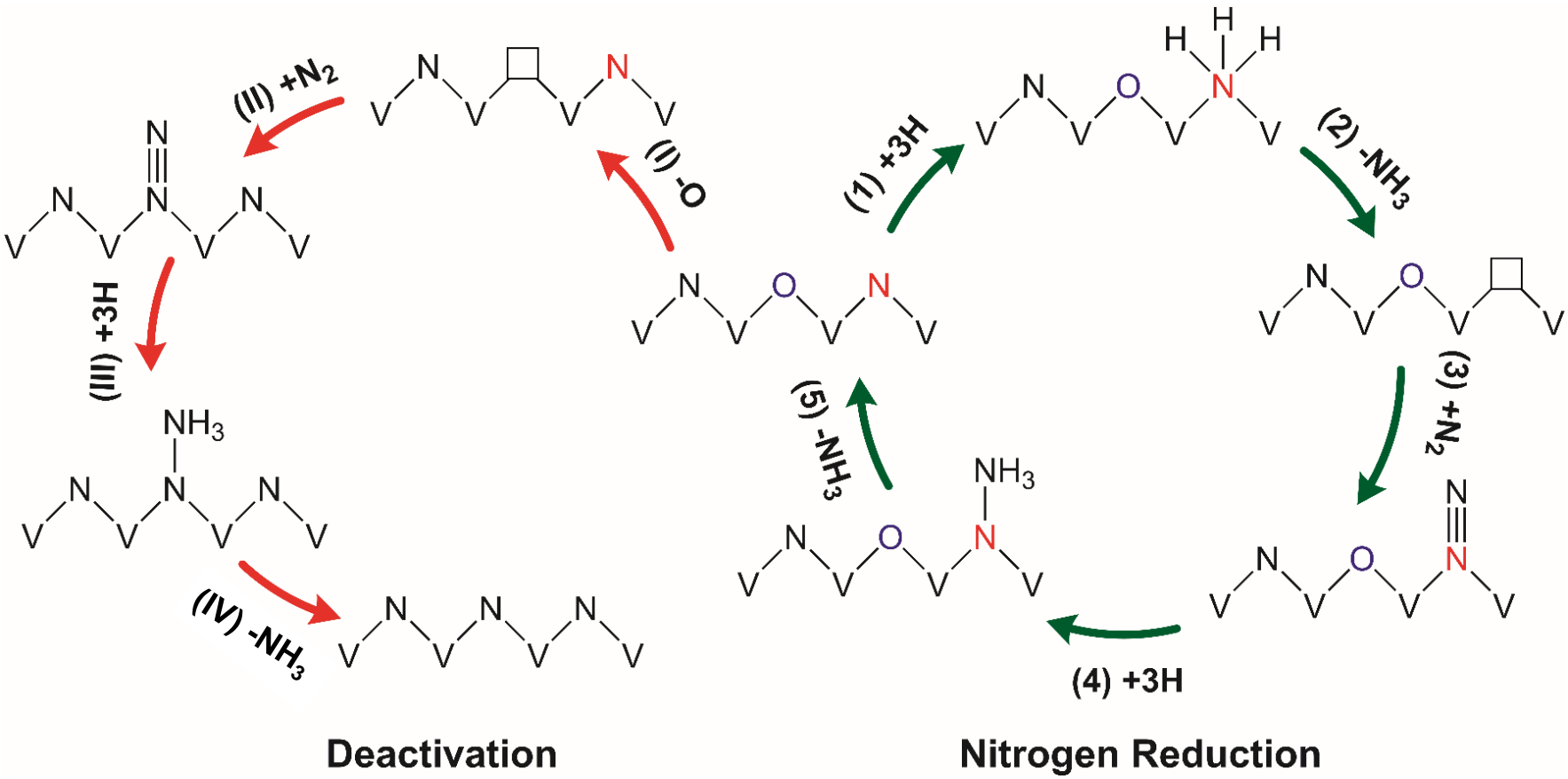

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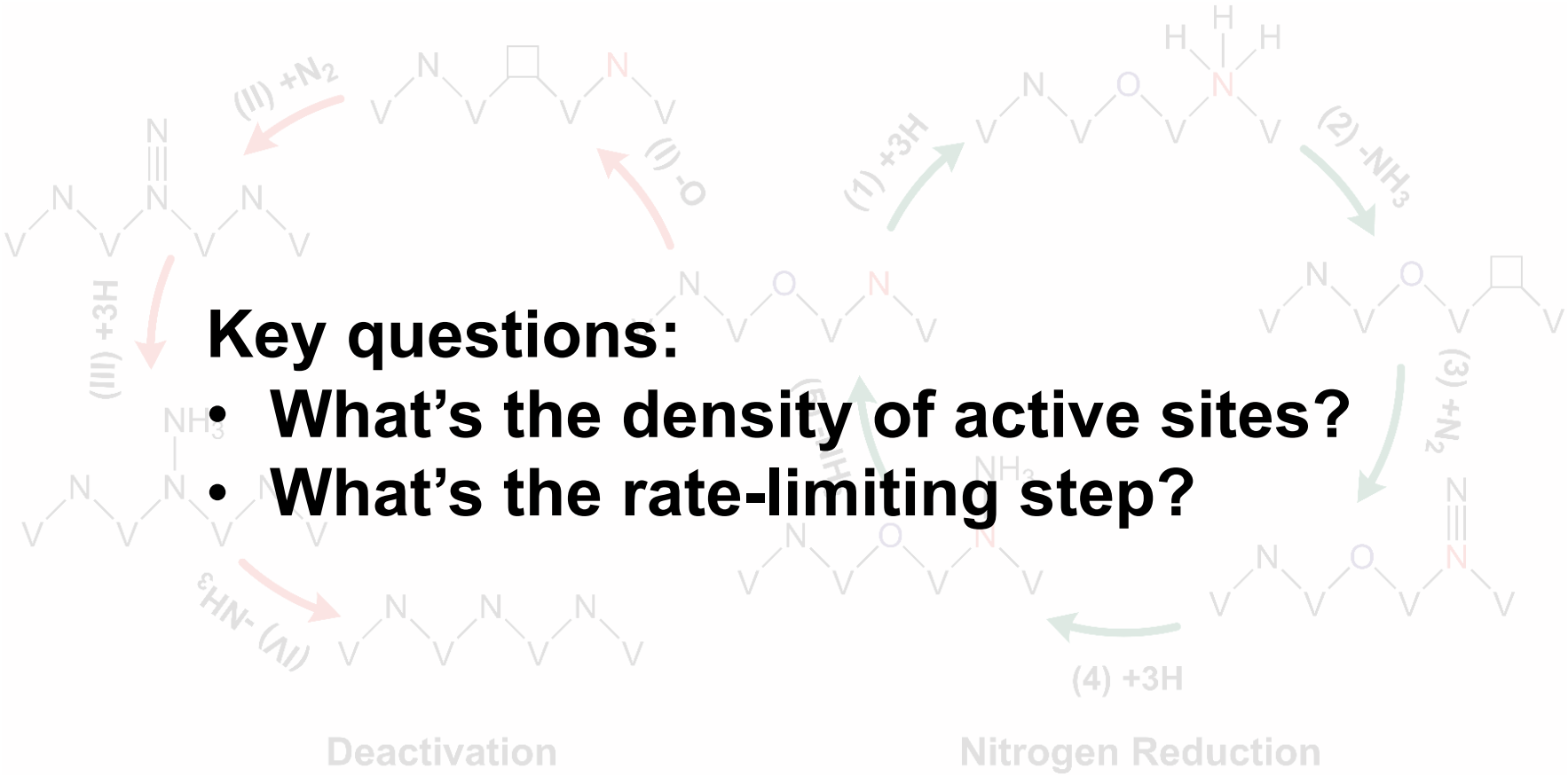

Key questions:

- **What's the density of active sites?**
- **What's the rate-limiting step?**

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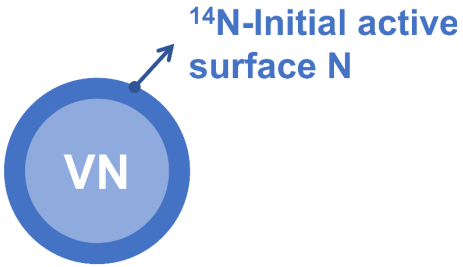
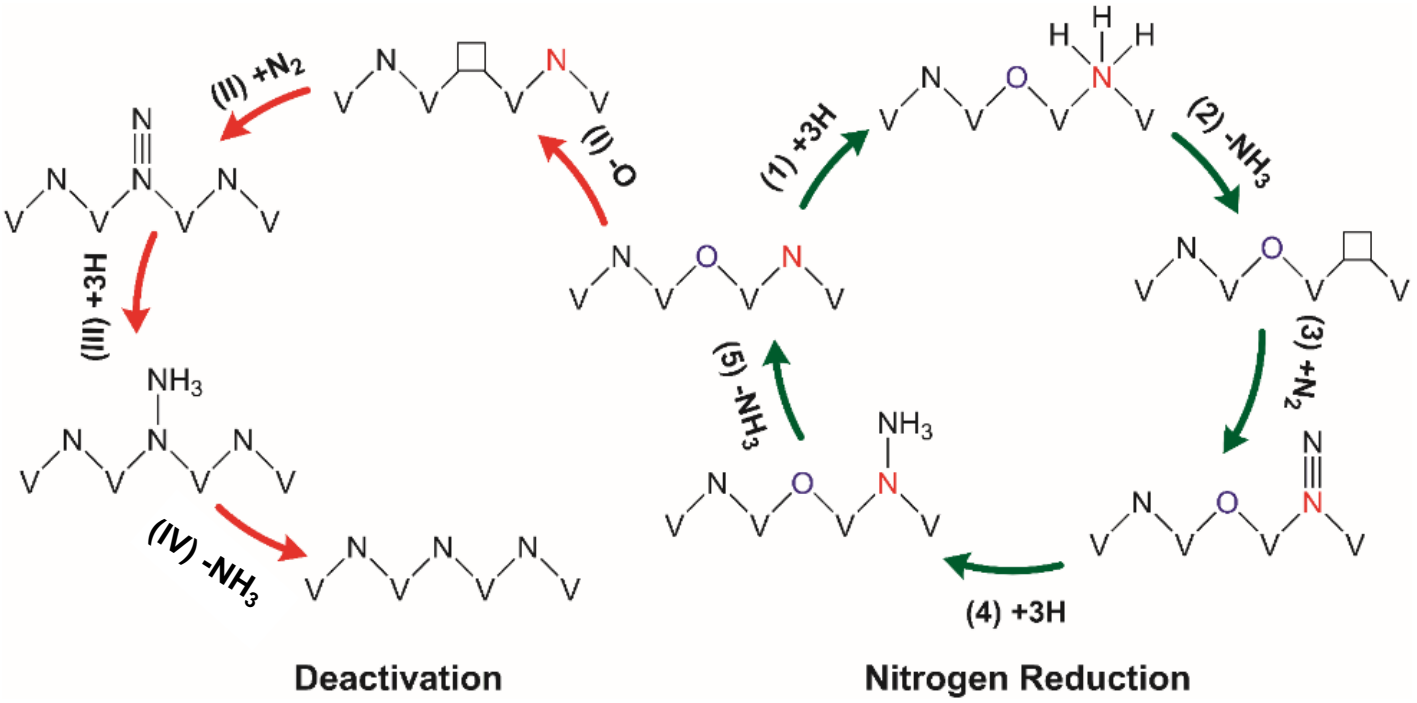
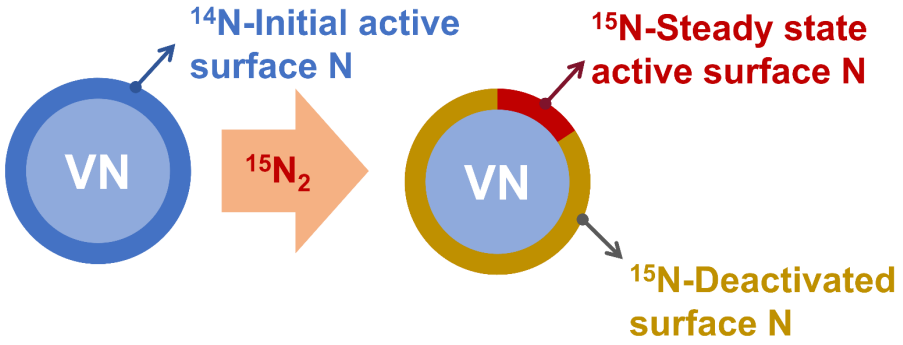
Density of Active Sites

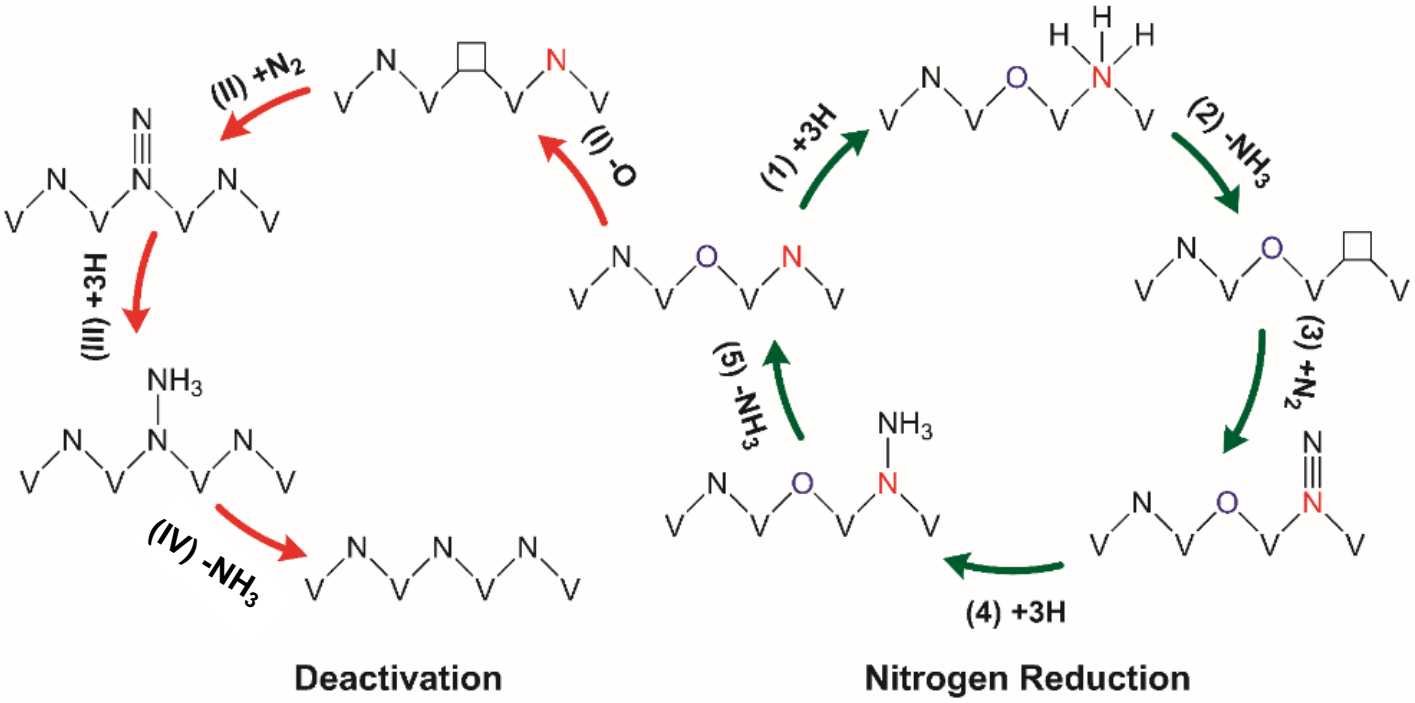




Yang et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 13768−13772

Density of Active Sites





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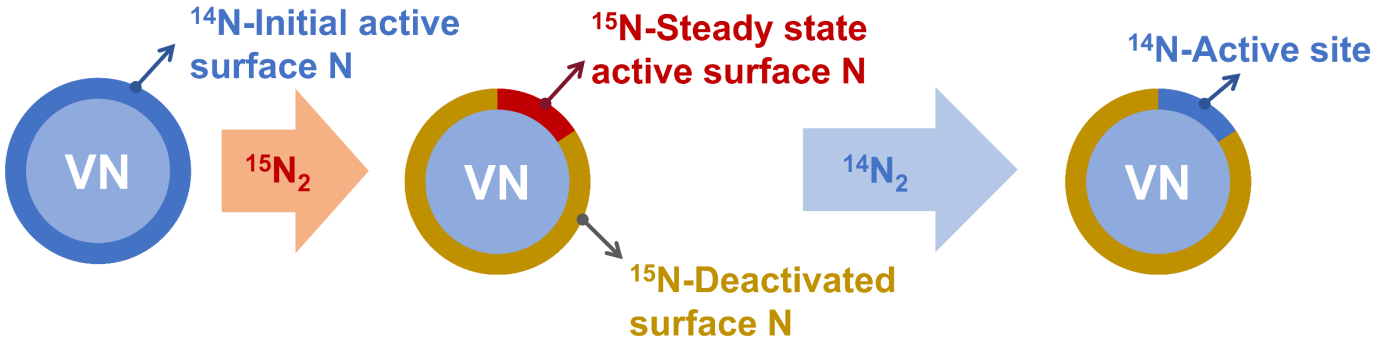
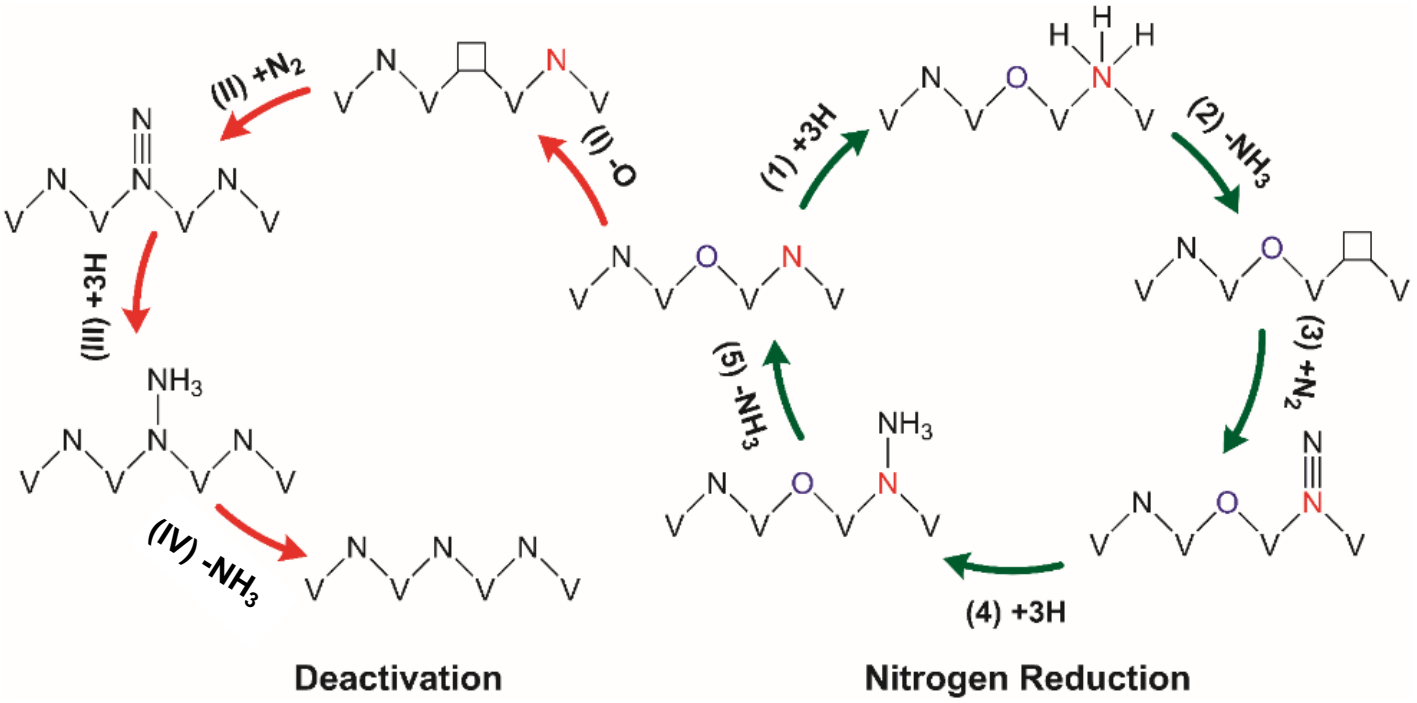
Density of Active Sites





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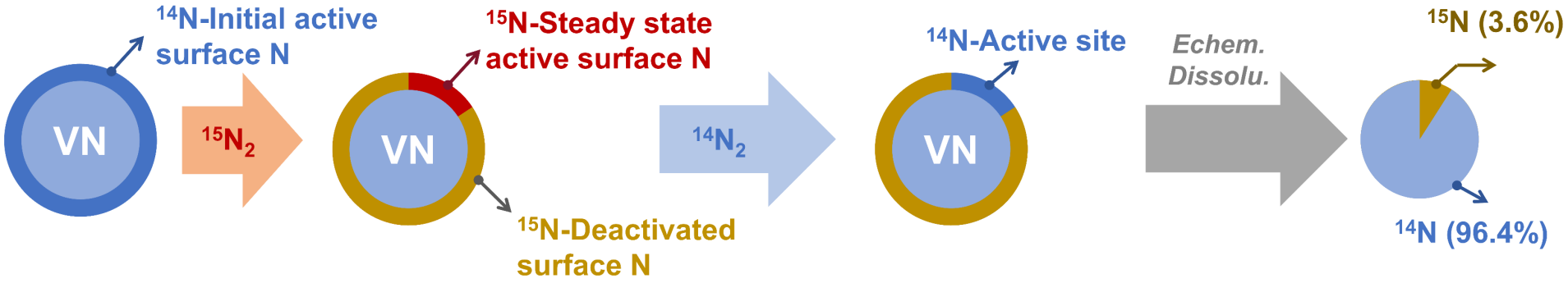
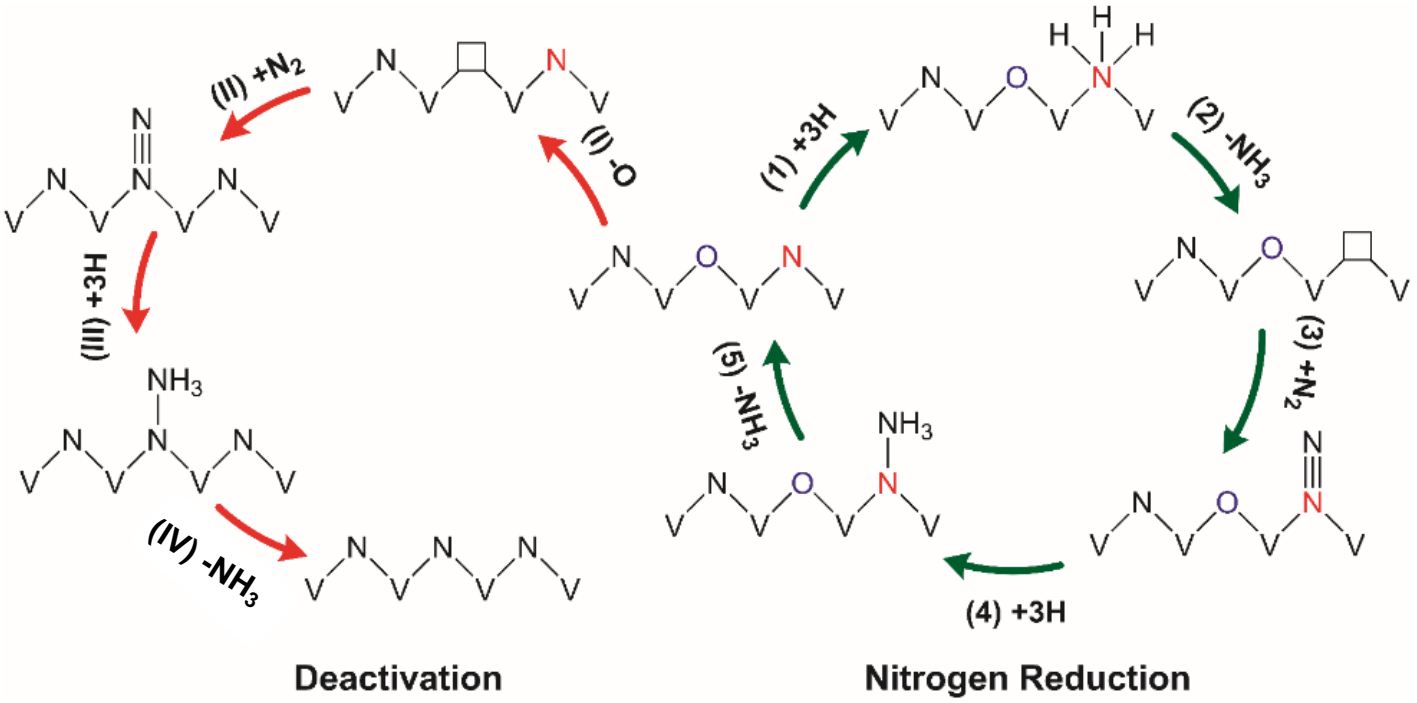
Density of Active Sites





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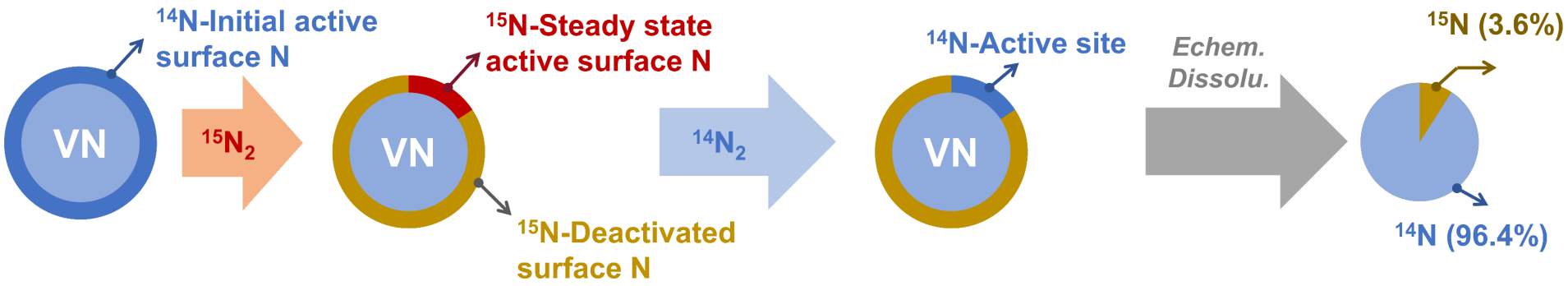
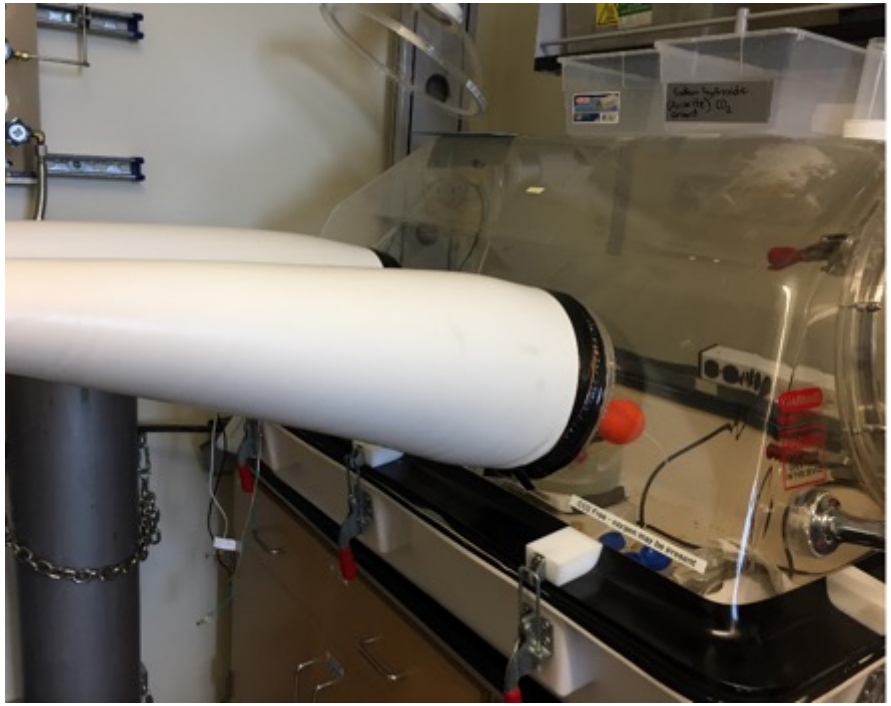
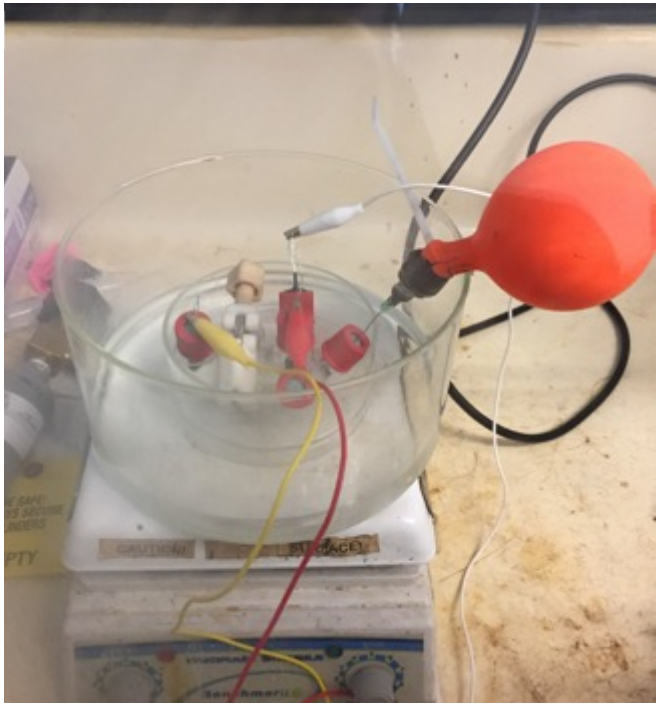
Density of Active Sites







Yang et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 13768−13772

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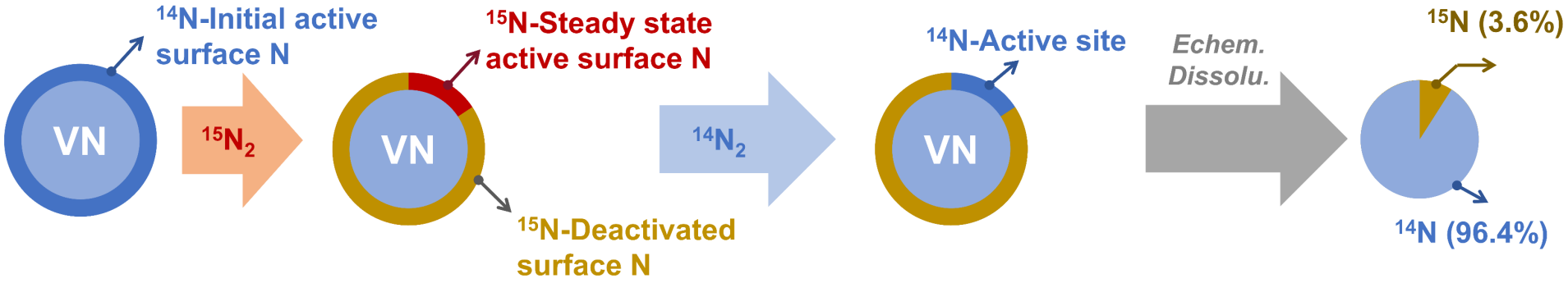

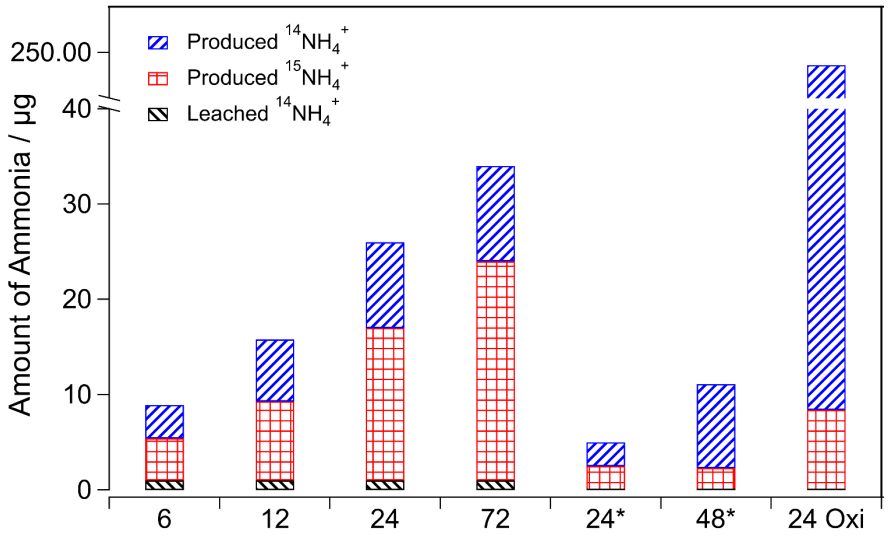

The density of initial active N atoms is about 4.2%, about 25% of the initially active surface N are able to sustain catalytic turnovers at the steady state

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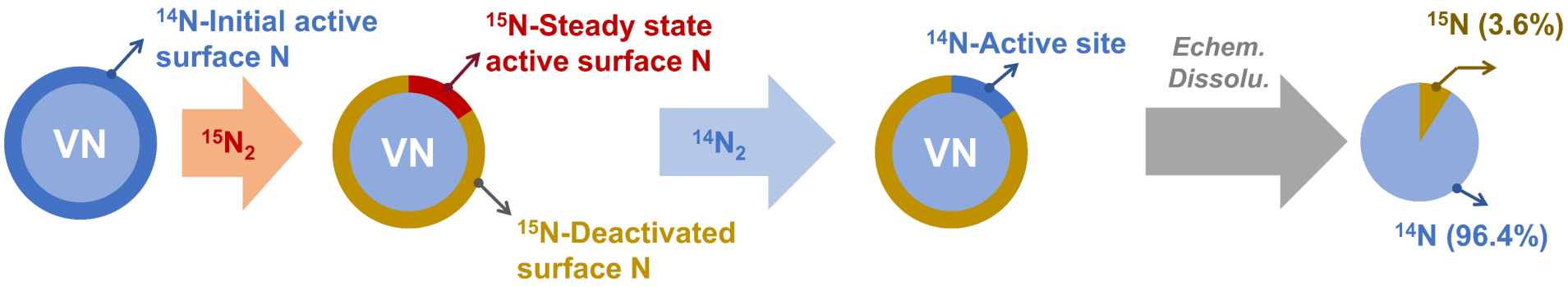

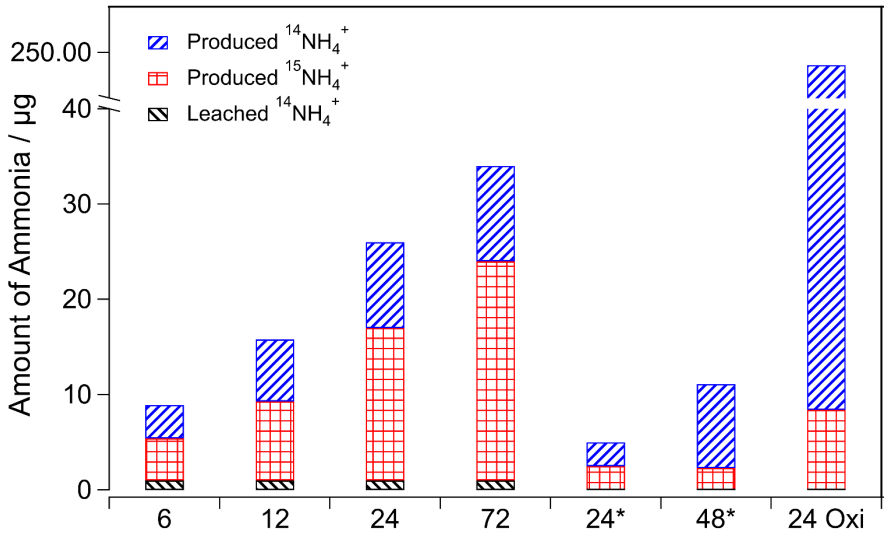

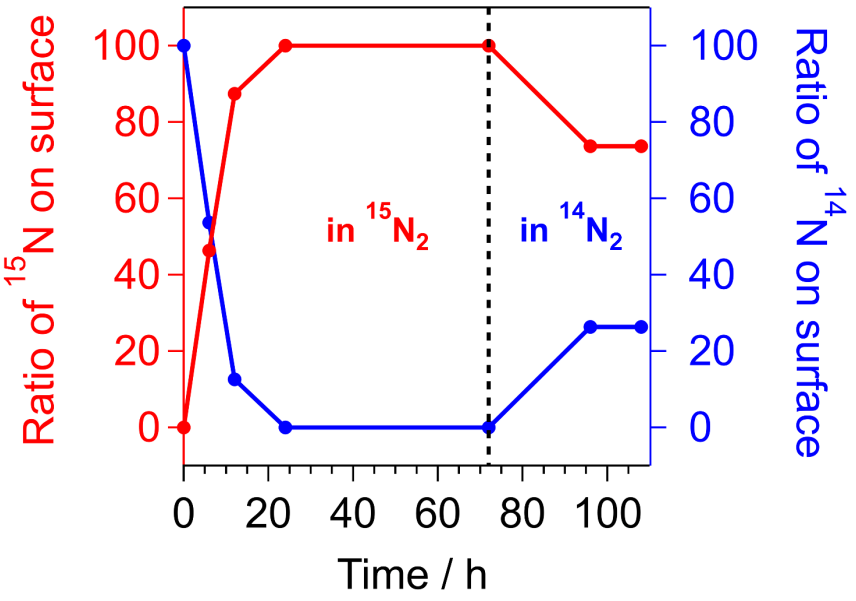

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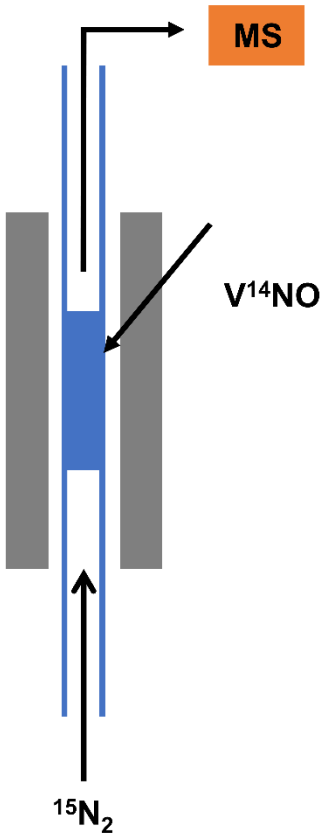
Yang et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 13768−13772

Activation Energy of ENRR



$$^{15}N_2 + V^{14}NO \longrightarrow V^{15}NO + {}^{14}N^{15}N$$

Yang et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 13768−13772

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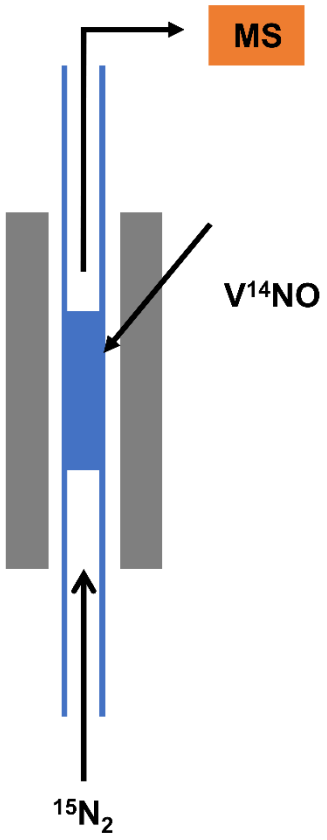

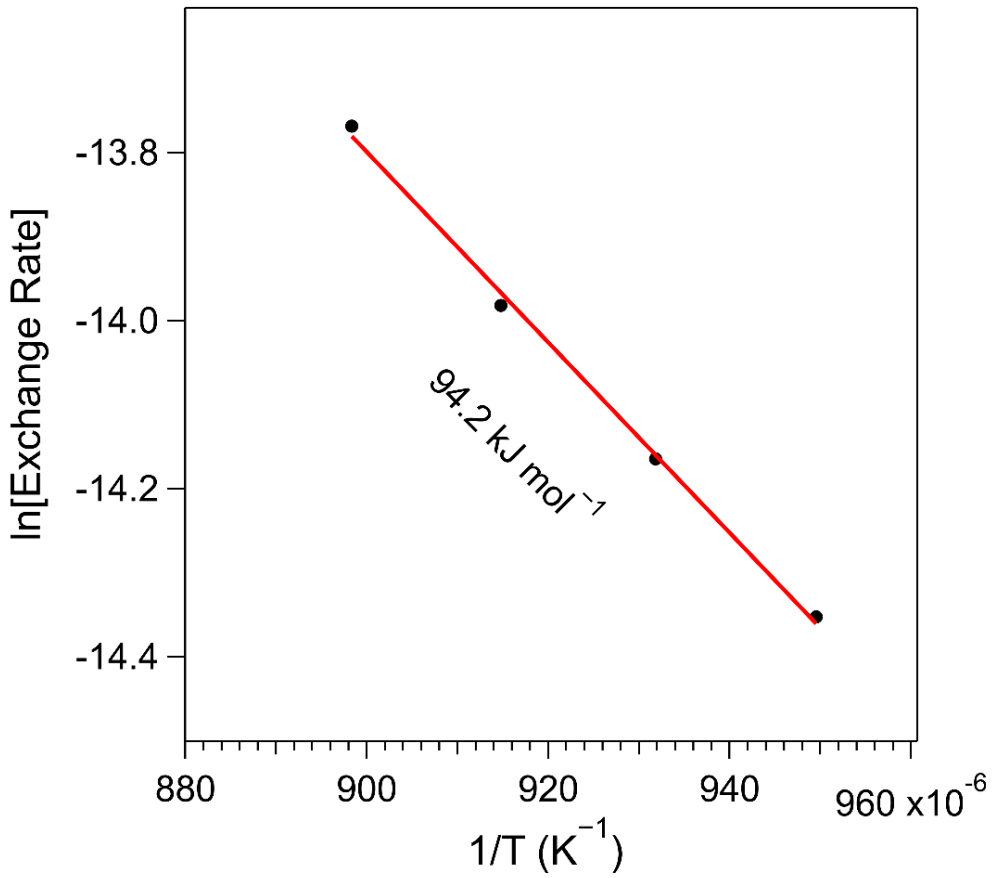

$^{15}N_2 + V^{14}NO \longrightarrow V^{15}NO + {}^{14}N^{15}N$

The activation energy is about 94.2 kJ mol^{-1}

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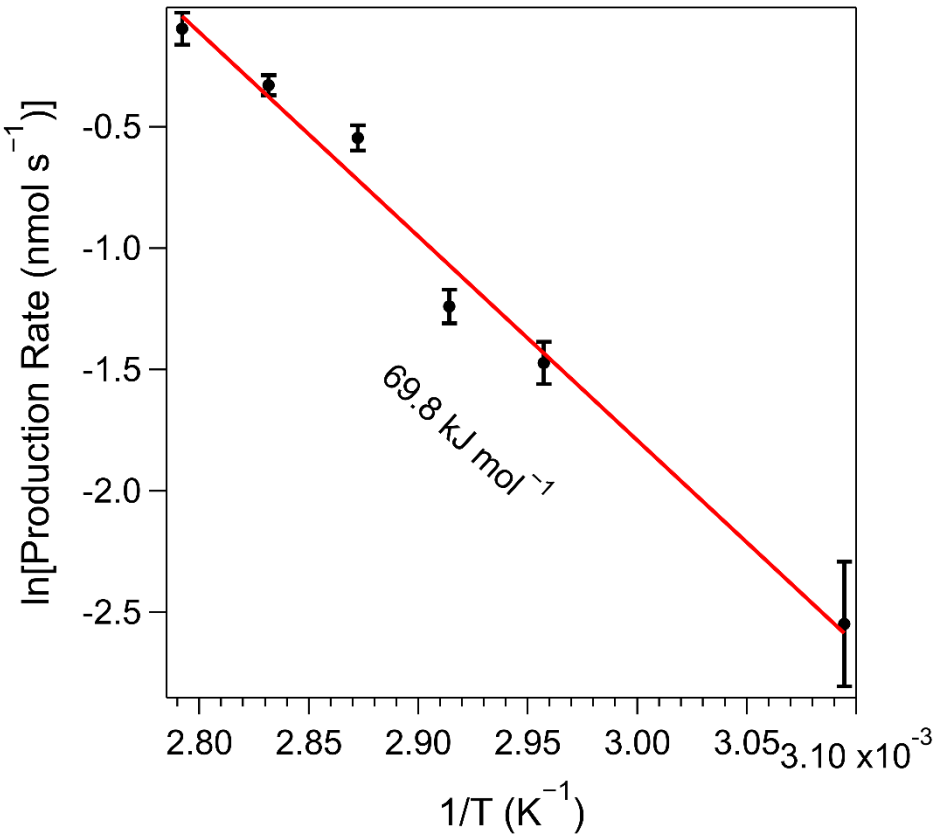

ΔE at −0.1 V vs RHE: 69.8 kJ mol^{-1}

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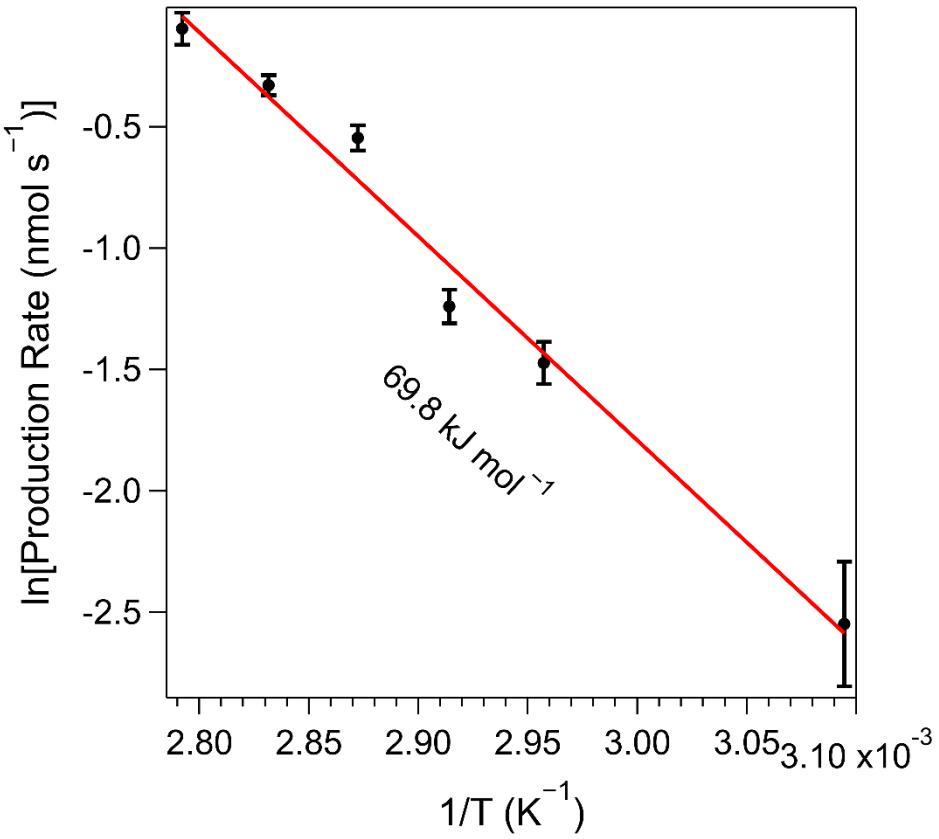

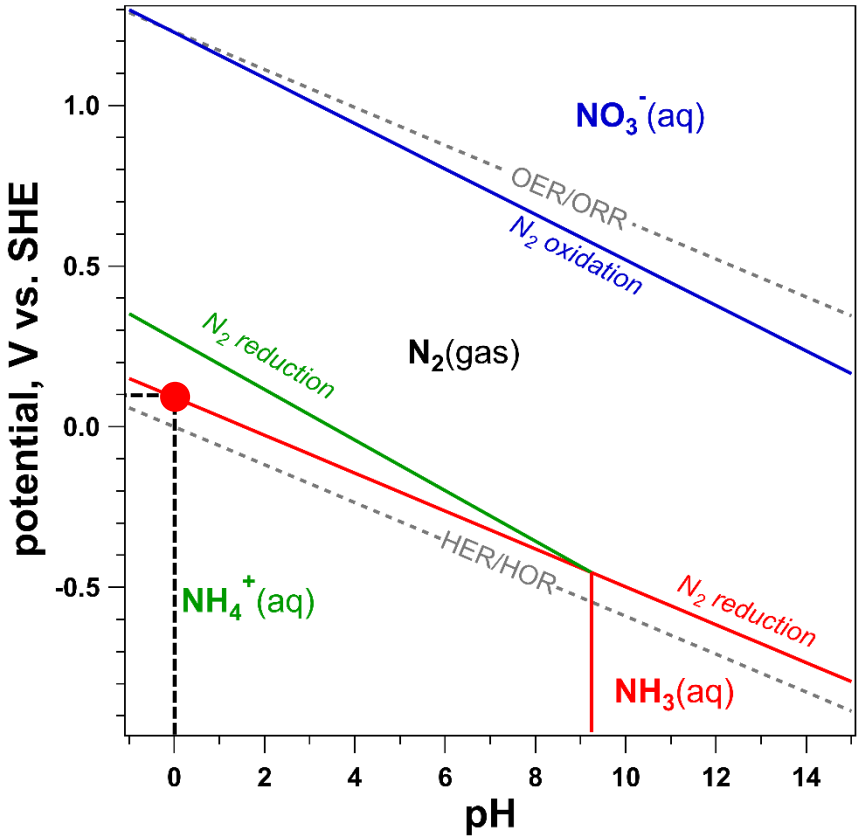

The activation energy at no overpotentials is:

96 kJ mol^{-1} eV^{-1} × 0.2 eV + 69.8 kJ mol^{-1} = 89 kJ mol^{-1}

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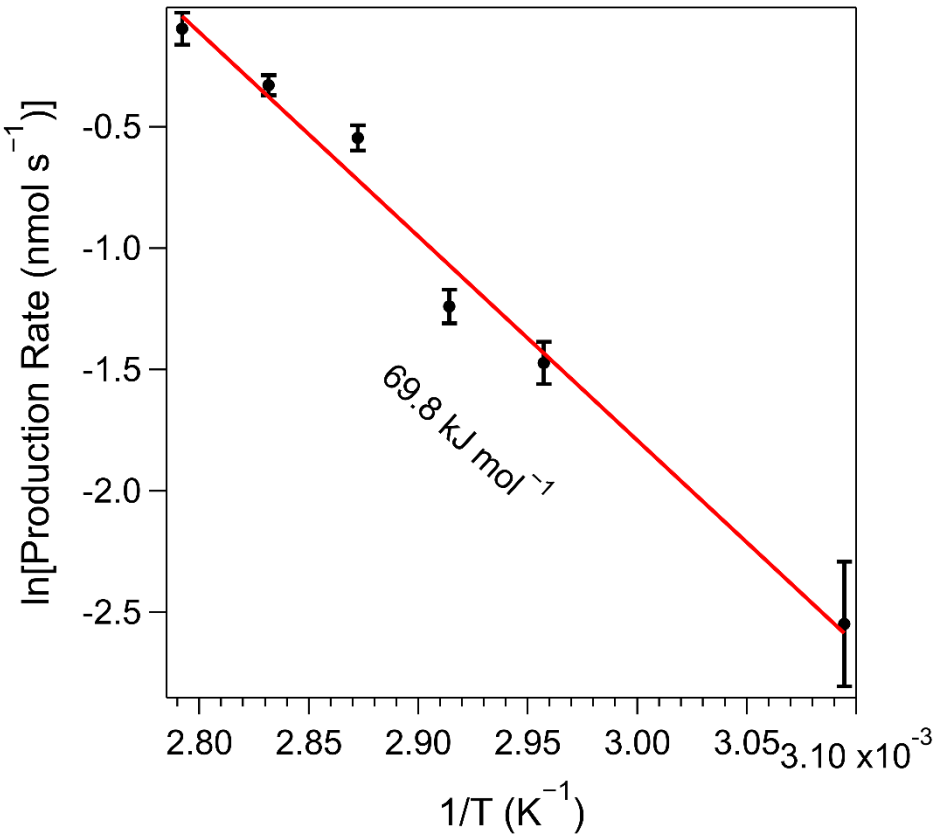

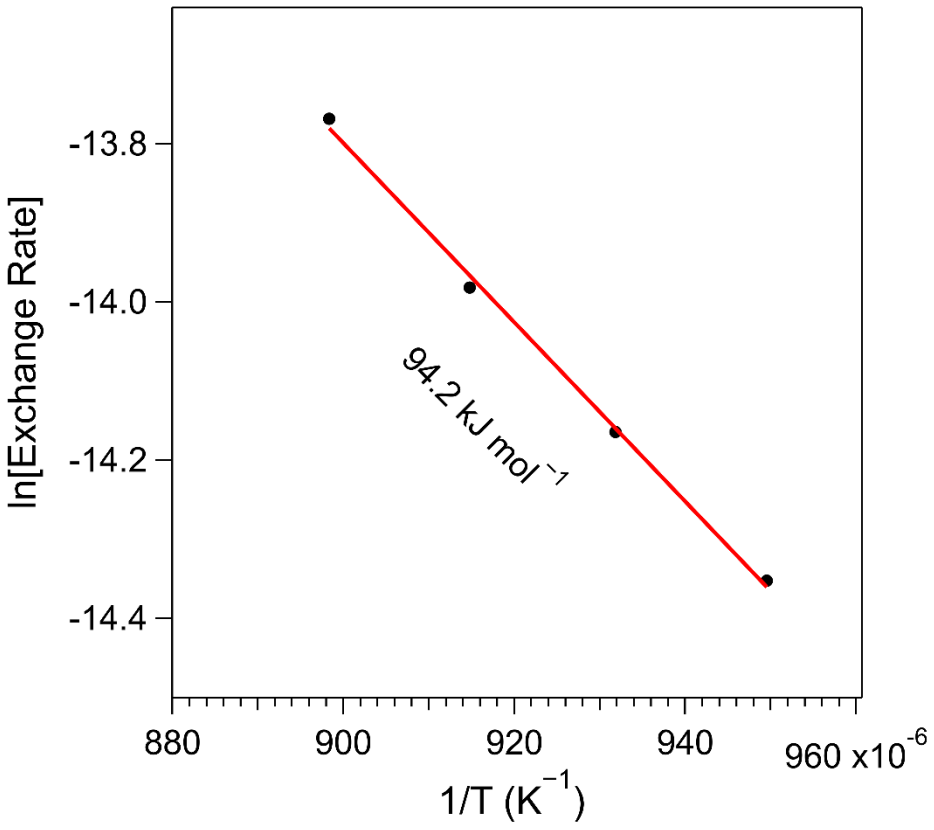

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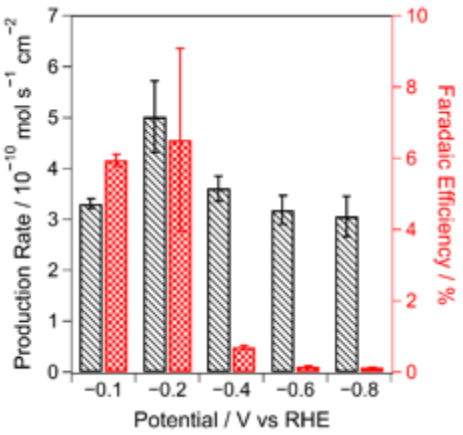
The activation of the N≡N bond on VNO is likely the shared rate limiting step in both thermochemical and electrochemical N_2 activation.

Yang et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 13768−13772

Conclusion

1. VN is an active, selective and stable ENRR Catalyst



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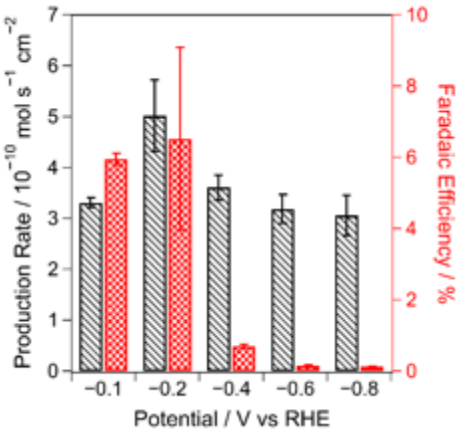

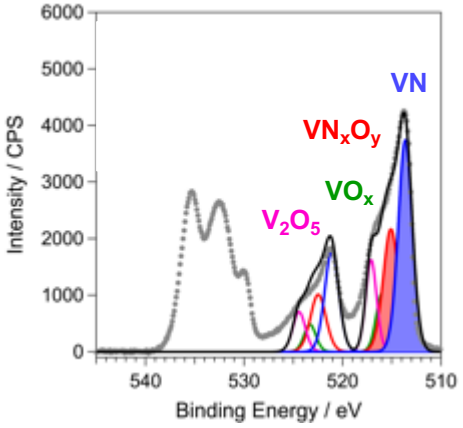

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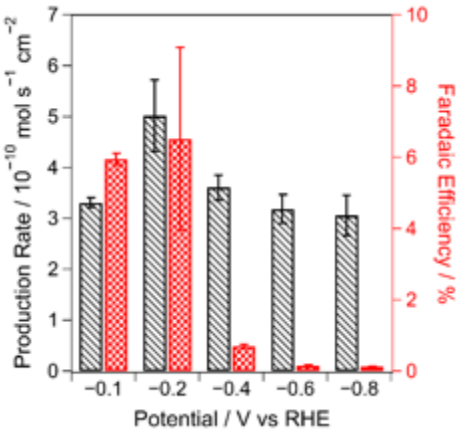

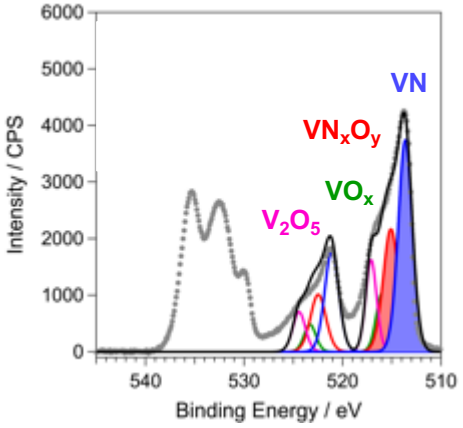

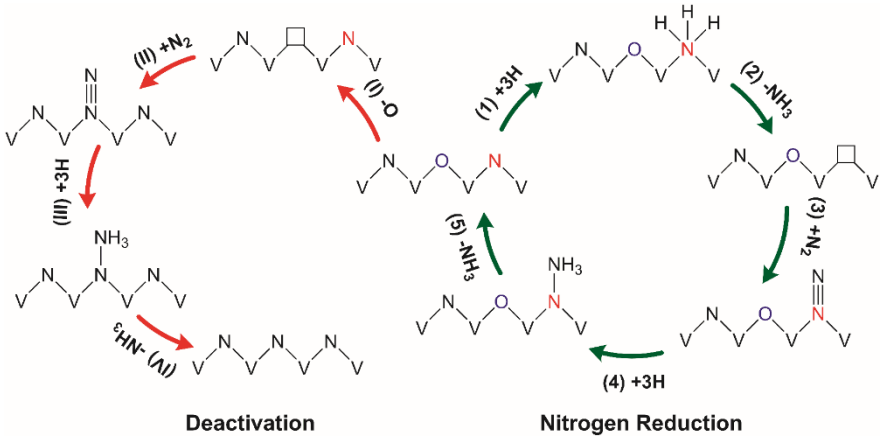

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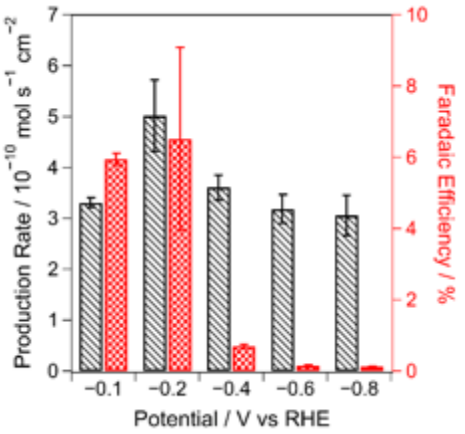

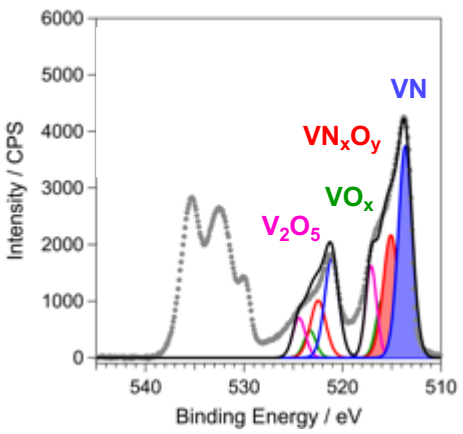

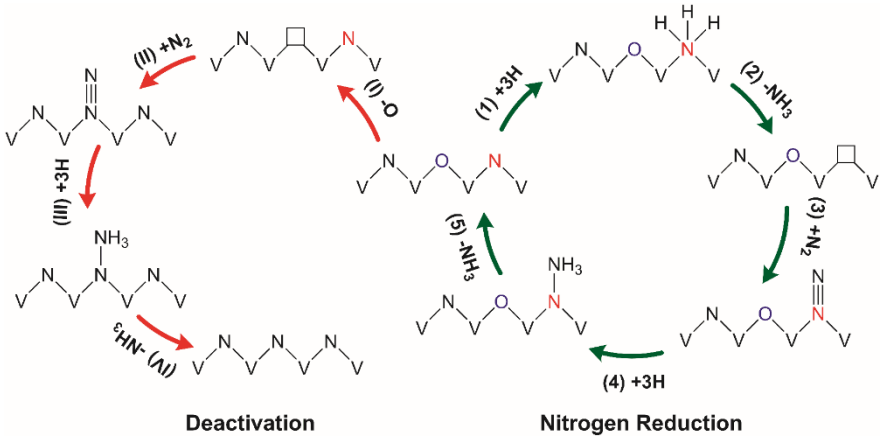

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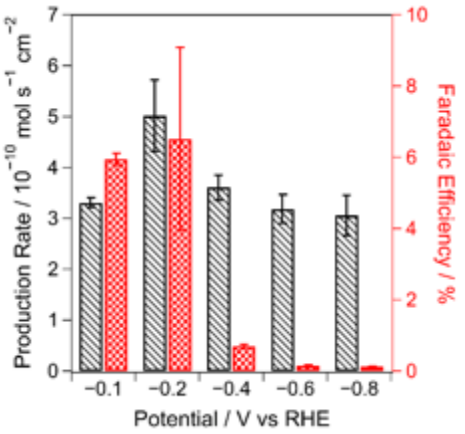
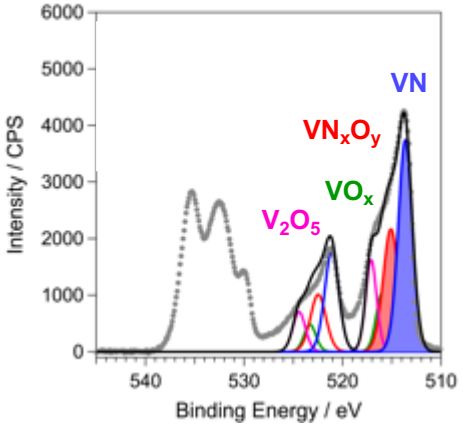
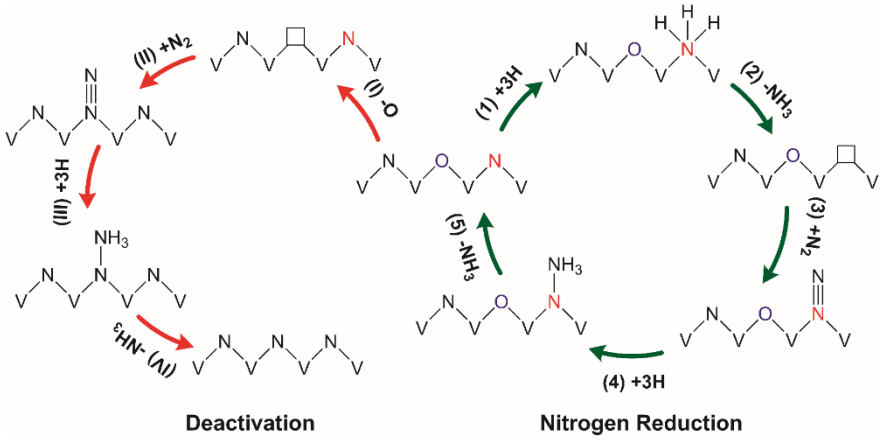
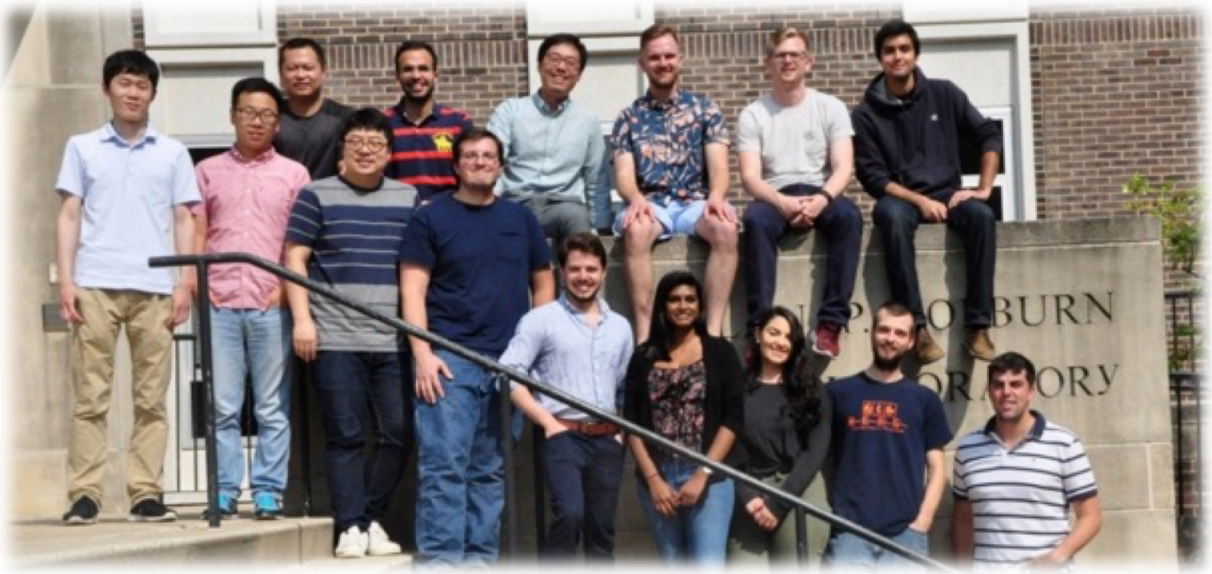


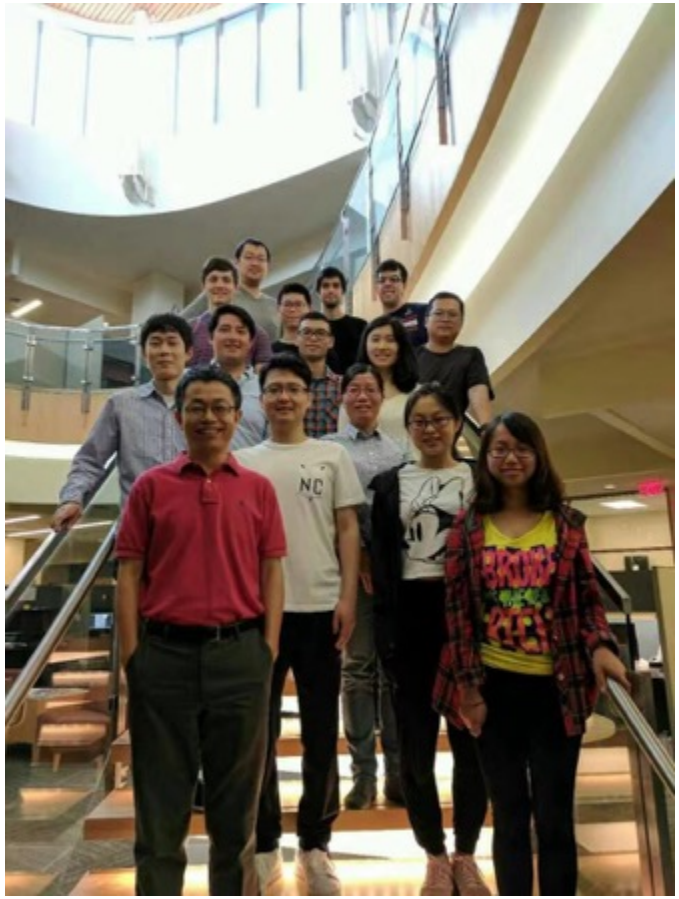




Acknowledgement



Xu Lab



Yan Lab

Collaborators

Prof. Jingguang G. Chen

Dr. Eli Stavitski

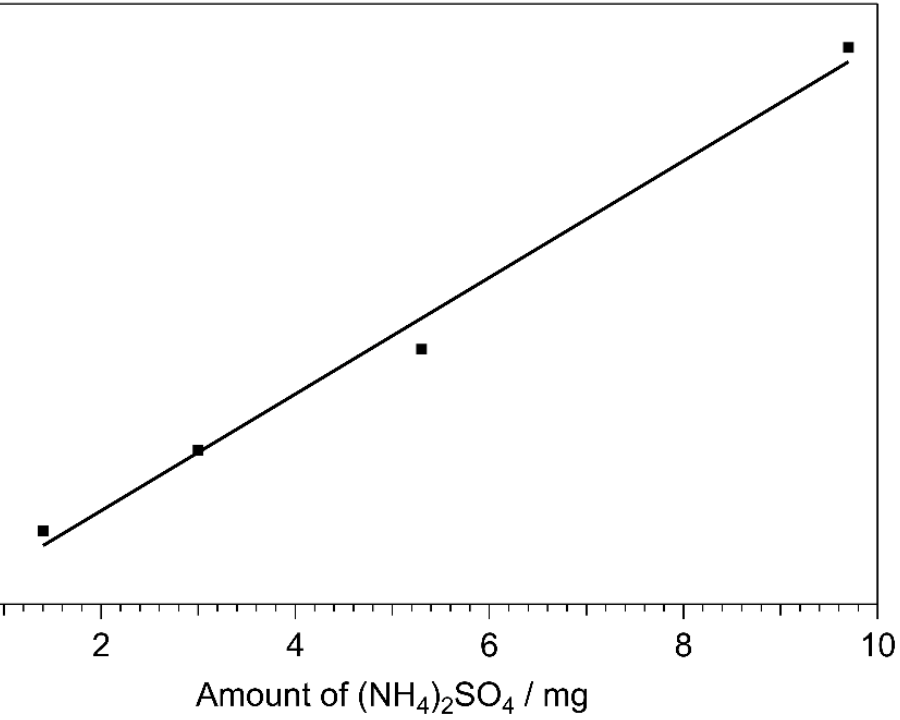
Dr. Klaus Attenkofer

U.S. DEPARTMENT OF ENERGY

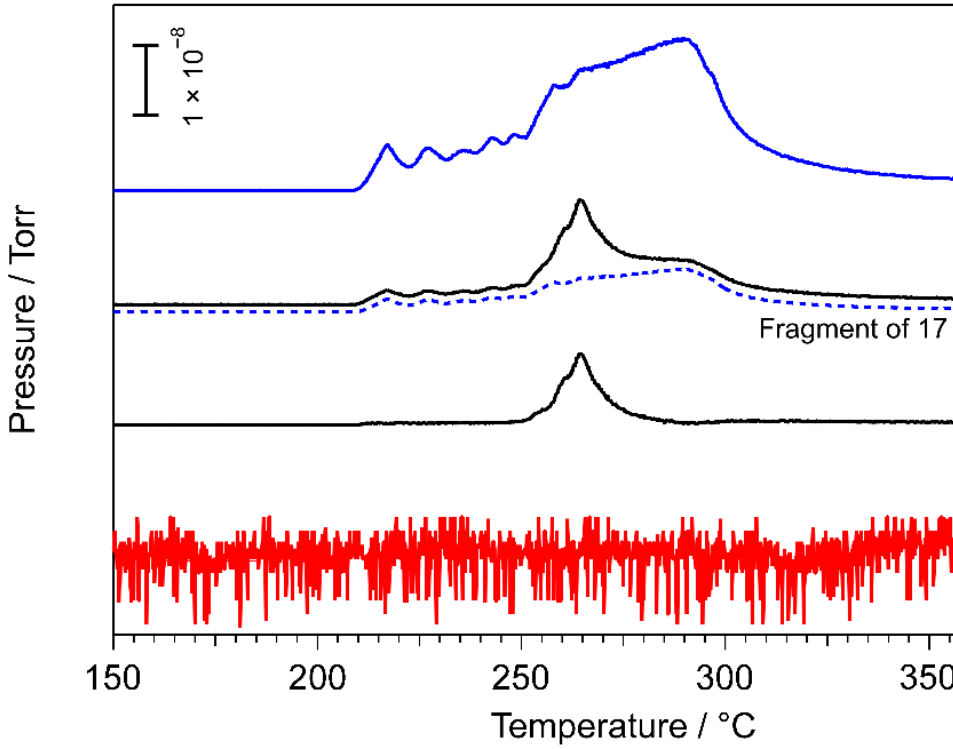
Thank you!

TPD-MS Quantification Agrees with Nessler's Method

Calibration



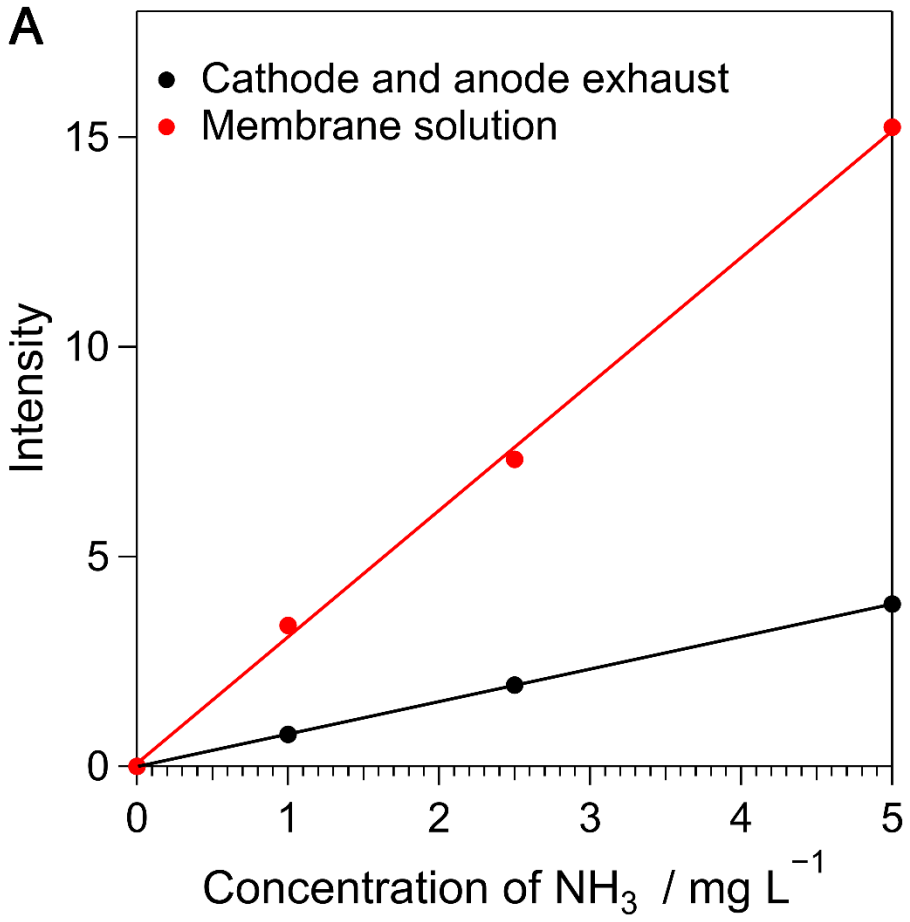
TPD-MS

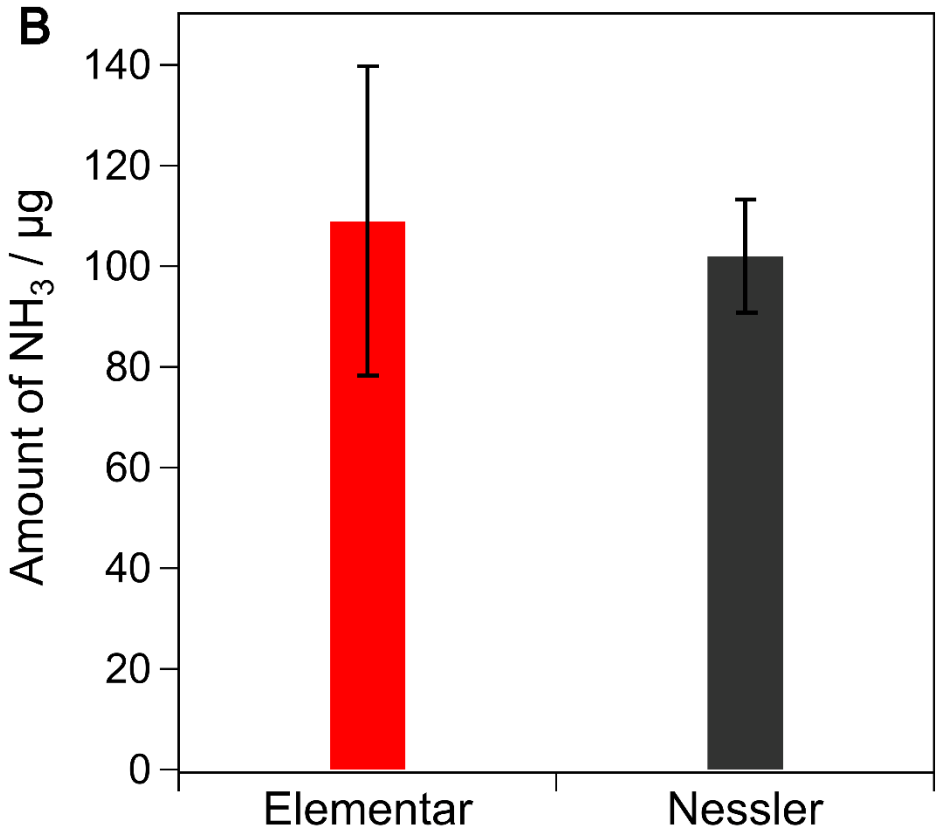


t of ammonia quantified by the Nessler's and TPD-MS are 3.2 mg and 2.9 mg, ively

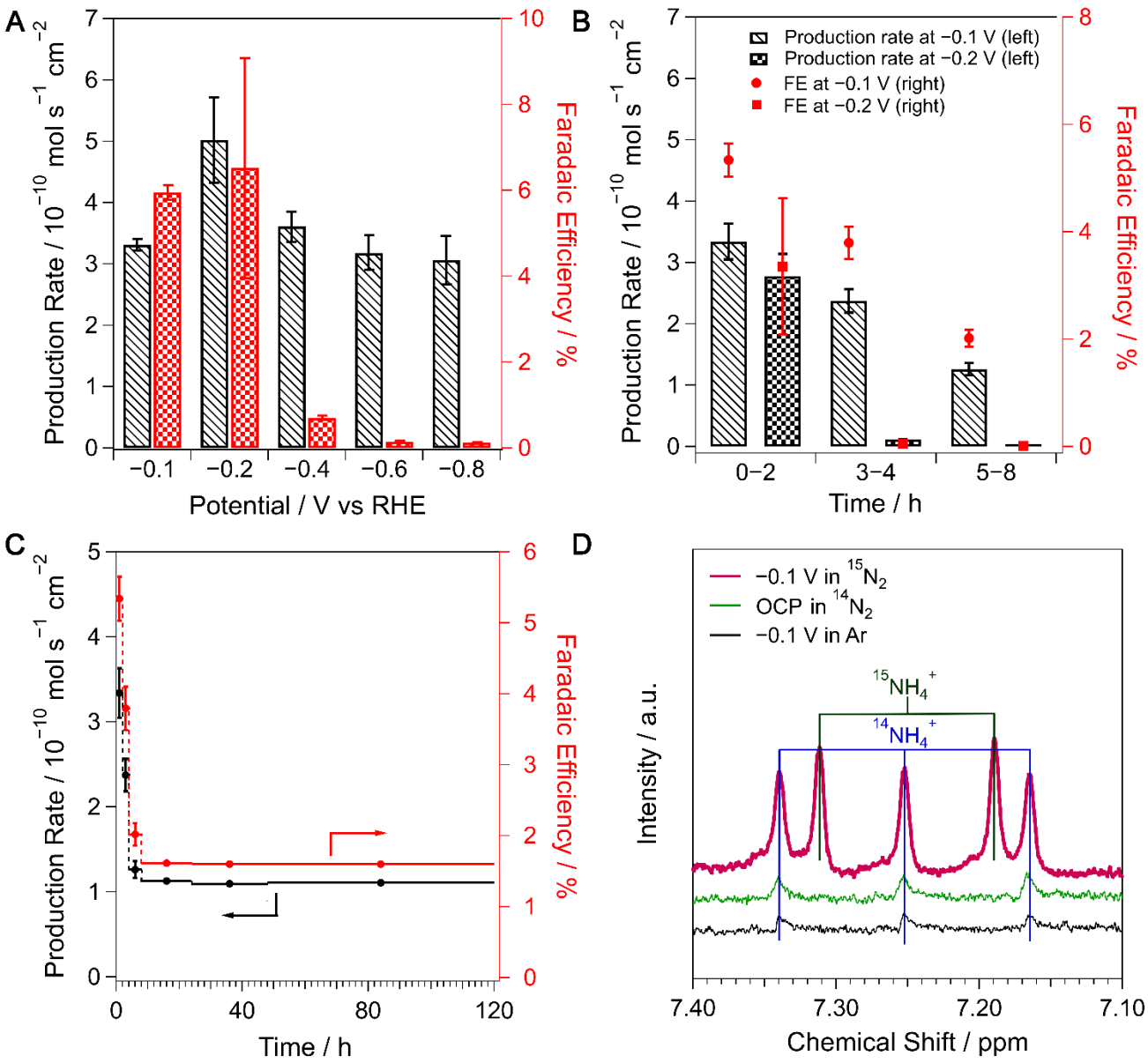
ENRR on VN at -0.1 V for 12

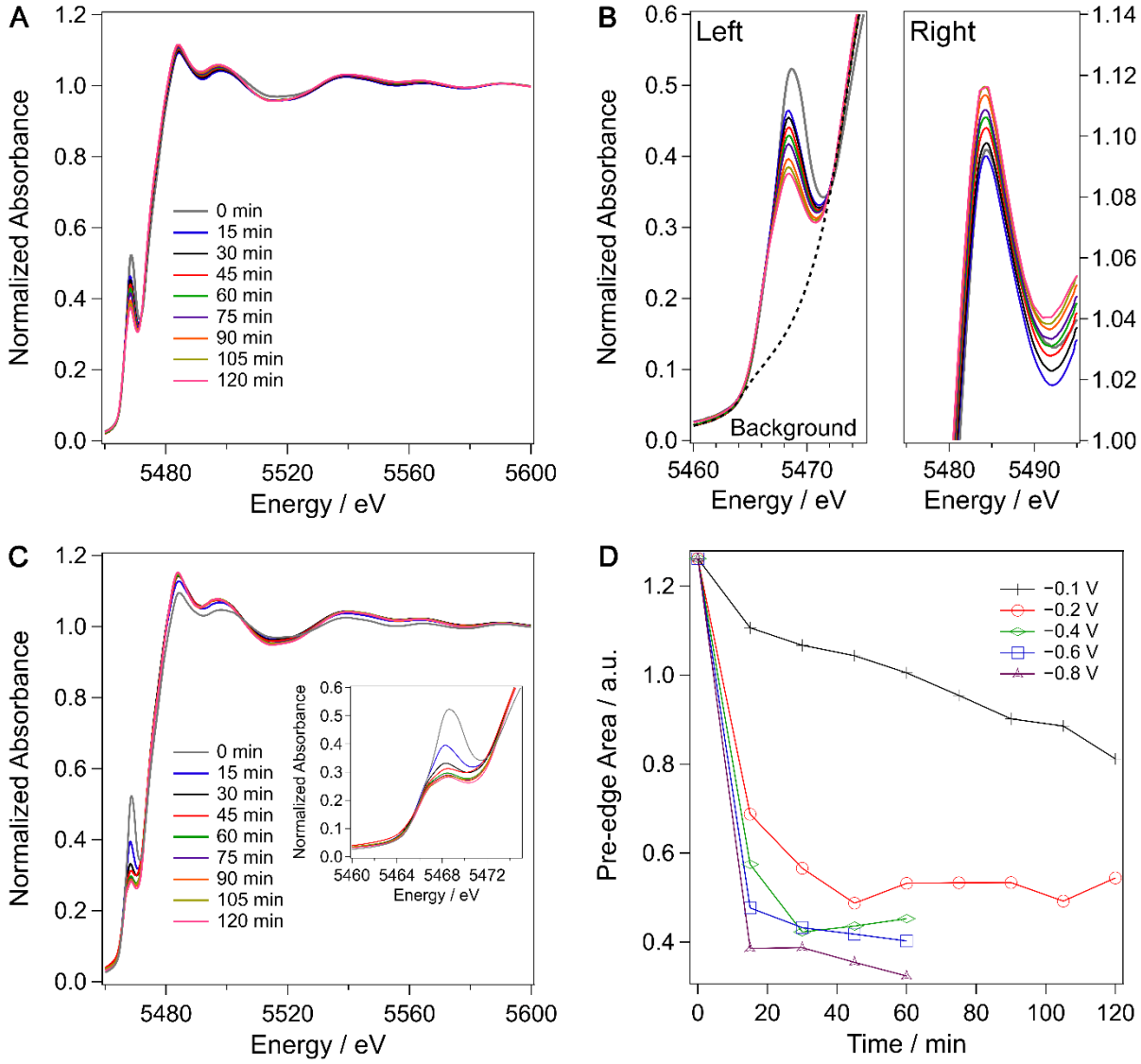
ntar Analysis Enables Accurate Quantification of Produced Am





t OCP, the Elementar results were consistent to Nessler results


A
Production Rate / 10^{-10} mol s^{-1} cm^{-2}
Faradaic Efficiency / %
−0.1
−0.2
−0.4
−0.6
−0.8
Potential / V vs RHE
B
Production rate at −0.1 V (left)
Production rate at −0.2 V (left)
FE at −0.1 V (right)
FE at −0.2 V (right)
Production Rate / 10^{-10} mol s^{-1} cm^{-2}
Faradaic Efficiency / %
0−2
3−4
5−8
Time / h
C
Production Rate / 10^{-10} mol s^{-1} cm^{-2}
Faradaic Efficiency / %
Time / h
D
−0.1 V in $^{15}N_2$
OCP in $^{14}N_2$
−0.1 V in Ar
$^{15}NH_4^+$
$^{14}NH_4^+$
Intensity / a.u.
Chemical Shift / ppm


A
Normalized Absorbance
Energy / eV
0 min
15 min
30 min
45 min
60 min
75 min
90 min
105 min
120 min
B
Left
Right
Background
Normalized Absorbance
Energy / eV
C
Normalized Absorbance
Energy / eV
D
Pre-edge Area / a.u.
Time / min
−0.1 V
−0.2 V
−0.4 V
−0.6 V
−0.8 V

Turnover Number (TON) in ENRR

ed on the Elementar analysis and TGA results, the total N and V contents in the catalysts was 1
nd 58.5 wt%, respectively.

ce there was 2.5 mg of the catalysts on carbon paper, the amounts of $VN_{0.7}O_{0.45}$ (d) and VN phas
determined to be 3.5 μmol and 25.2 μmol, respectively.

$$0.7 \times d + e = \frac{2.5\times10^{-3}\times15.51\%}{14}$$

$$d + e = \frac{2.5\times10^{-3}\times58.5\%}{50.9}$$

S results suggest that the accessible amount of $VN_{0.7}O_{0.45}$ was 57.8%, therefore, the TON of the
sts within 120 h is:

$$\frac{253.1\ \mu mol}{3.5 \times 0.7\ \mu mol \times 57.8\%} = 179$$

Overall TON

S results suggest that 35.7% of $VN_{0.7}O_{0.45}$ was converted to VN at −0.1 V for 2 h. Thus, the total
nt of active nitrogen atoms in the catalysts after 4 h was:

$$3.5 \times (57.8\% - 35.7\%) \times 0.7\ \mu mol = 0.54\ \mu mol$$

ce the total amount of ammonia produced at −0.1 V from 5 to 120 h was determined to be 232.5
the turnover number (TON) of the catalysts at steady state (5−120 h) was determined to be:

$$\frac{232.5\ \mu mol}{0.54\ \mu mol} = 431$$

Steady State TON