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Novel Catalyst Materials for Increasing Sulfur Tolerance in Solid Oxide Fuel Cells (Year 3 Final)

17 JUNE 2024

POC:	Talia Marie Sebastian, PhD
POC:	Theodore Burye, PhD

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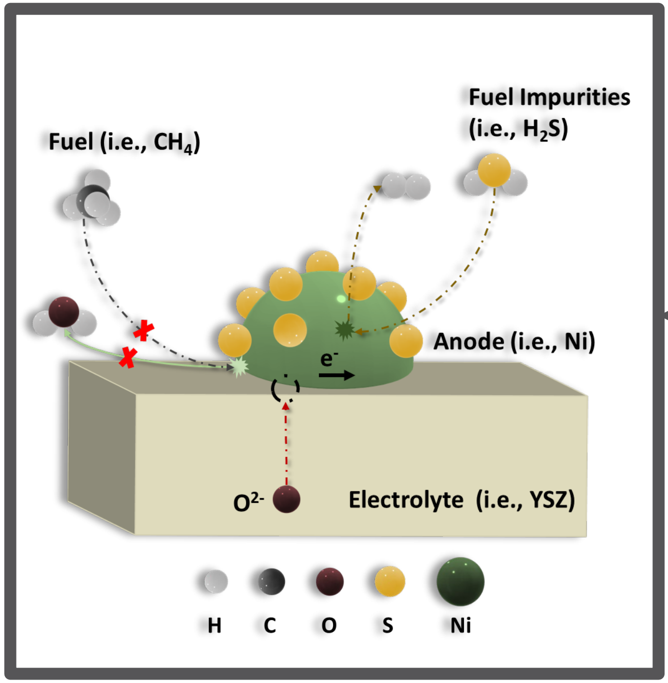
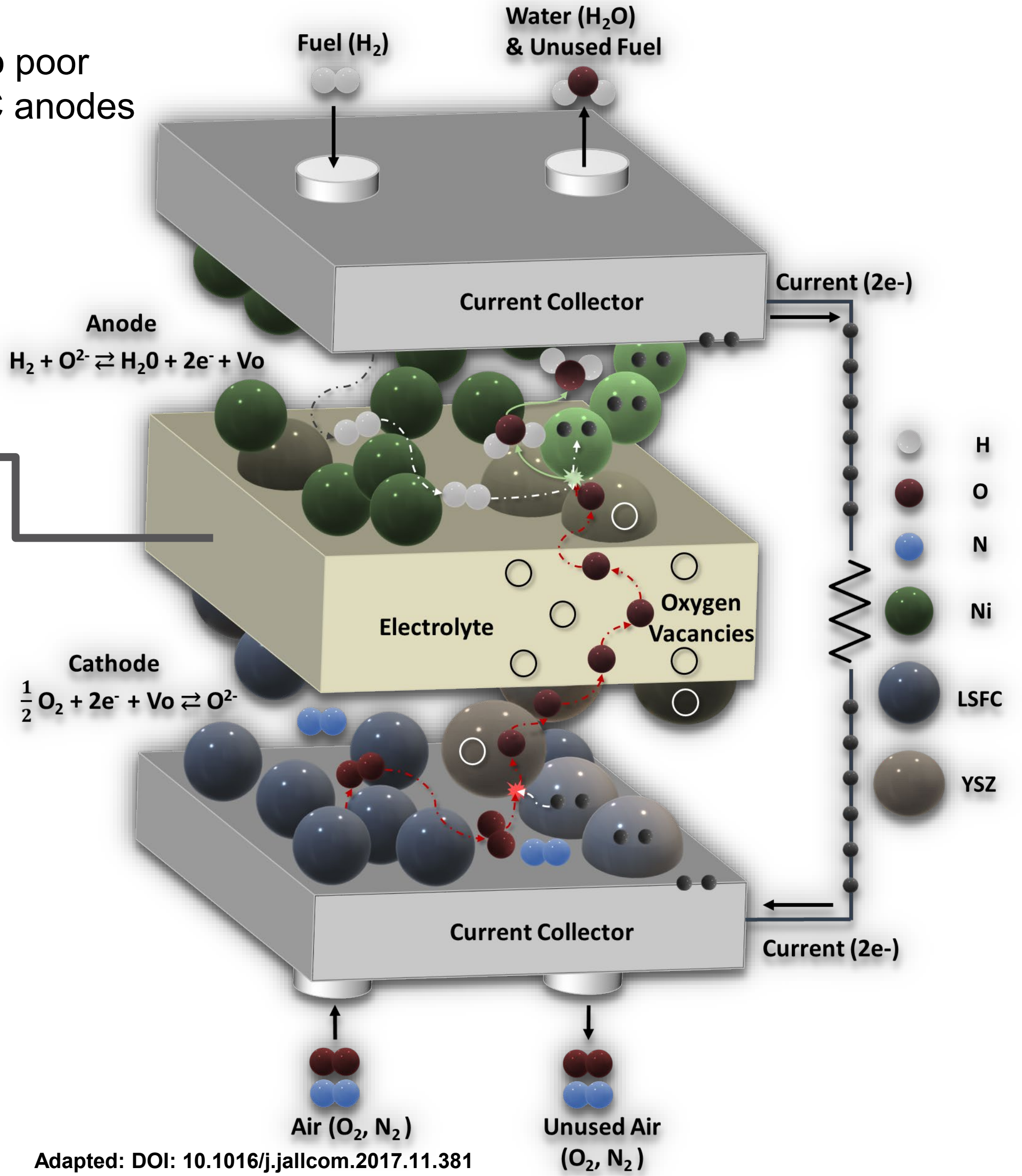
Introduction to Research Problem

Fuel Flexibility and Sulfur Poisoning

- Poisoning from sulfur impurities in fuel leads to poor performance and degradation of current SOFC anodes





Adapted: DOI: 10.1016/j.jallcom.2017.11.381

Mechanism of Chemisorption:

$$H_2S_{(g)} \leftrightarrow HS_{(ads)} + H_{(g/ads)} \leftrightarrow S_{(ads)} + H_{2(g)}$$

Mechanism of Sulfidation:

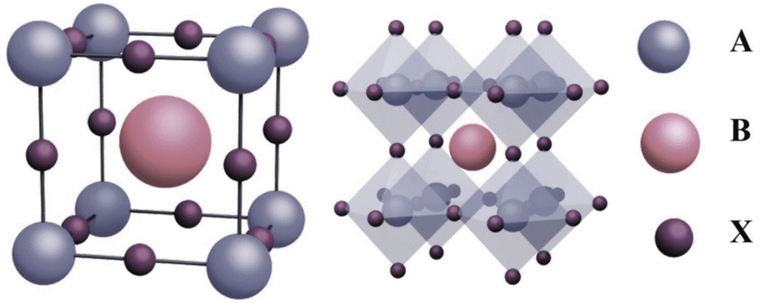
$$Ni_{(s)} + H_2S_{(g)} \leftrightarrow NiS_{(s)} + H_{2(g/ads)}$$

$$3Ni_{(s)} + xH_2S_{(g)} \leftrightarrow Ni_3S_{x(s)} + xH_{2(g)}$$

Experimental Approach to Research Problem

Materials-Based Mitigation Strategies

- Alloying nickel with noble or base metals
- Replacing nickel with base metals or nonmetal electronic conductors
- Replacing with mixed ionic-electronic conductors (i.e., Perovskite Oxides)

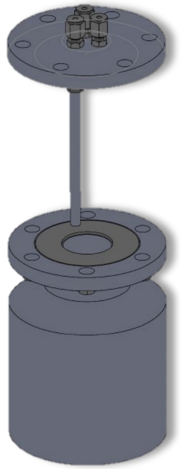


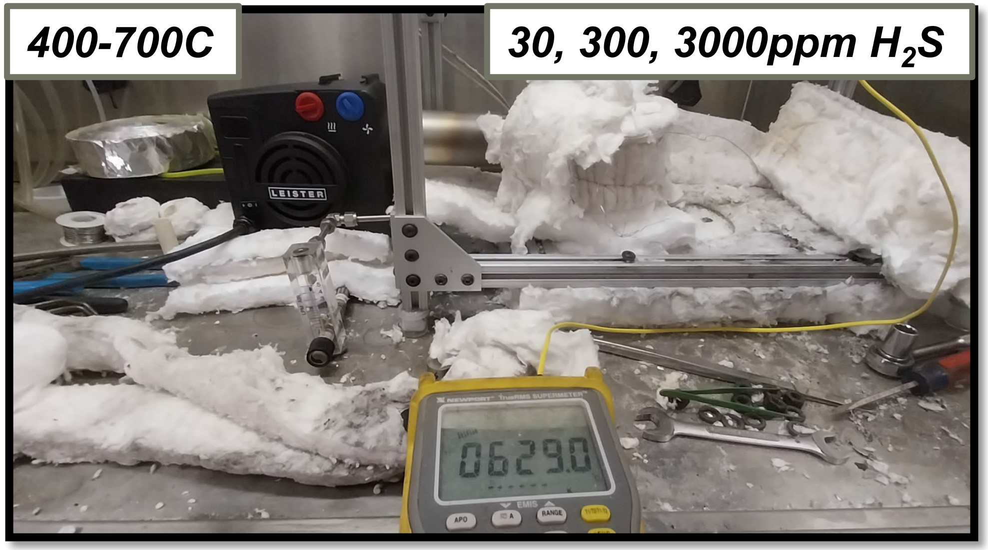
Adapted: DOI: 10.1002/advs.201700256

Lanthanum Strontium Vanadate

$La_{0.7}Sr_{0.3}VO_{3.85-\delta}$ (LSV)

~5g LSV



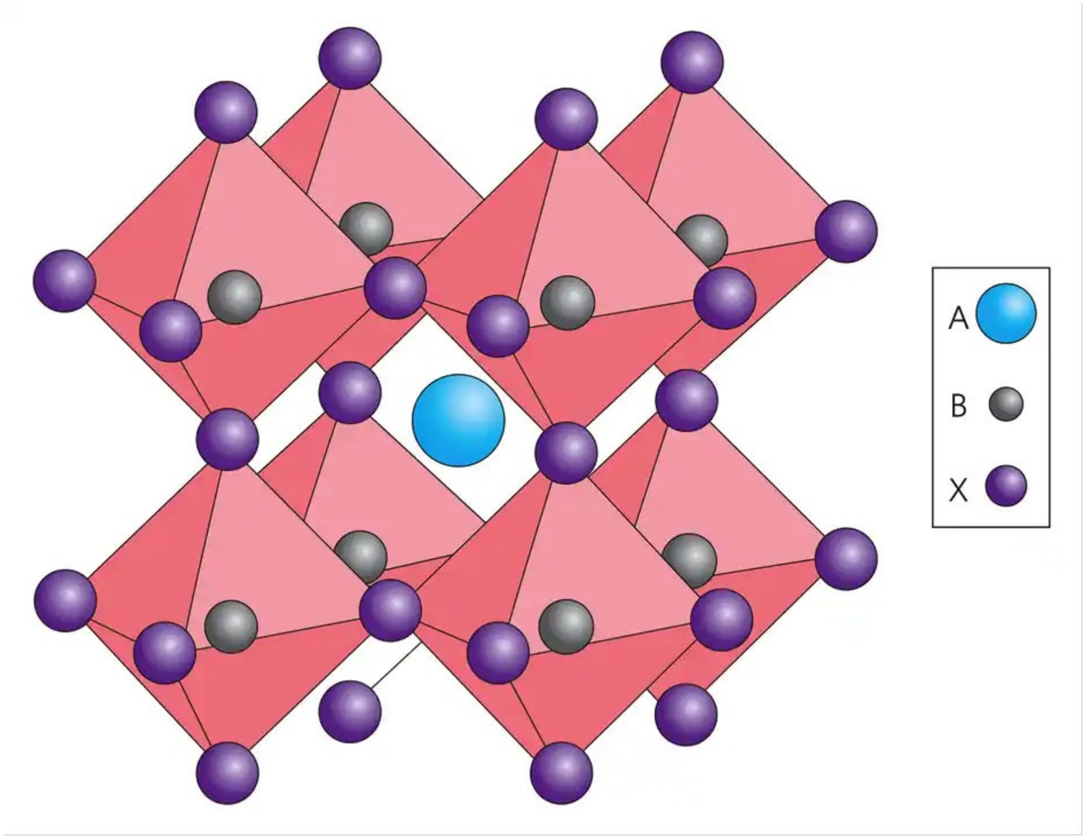


400-700C

30, 300, 3000ppm H_2S

Motivation– Perovskite and SOFC Materials

SOFC Catalysts - Perovskite (ABX_3)

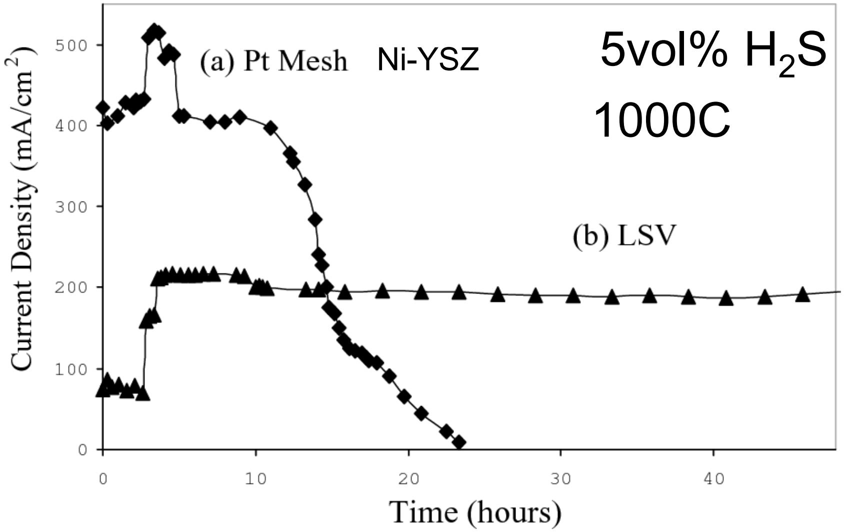


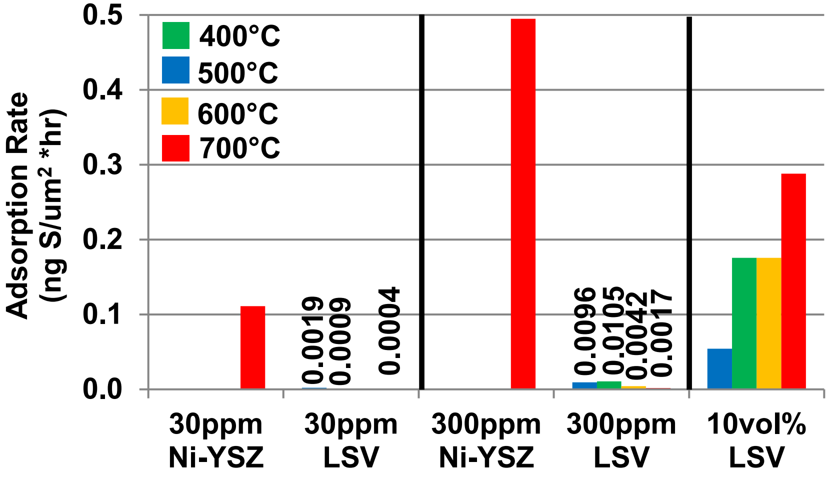
Common Catalyst Formulations

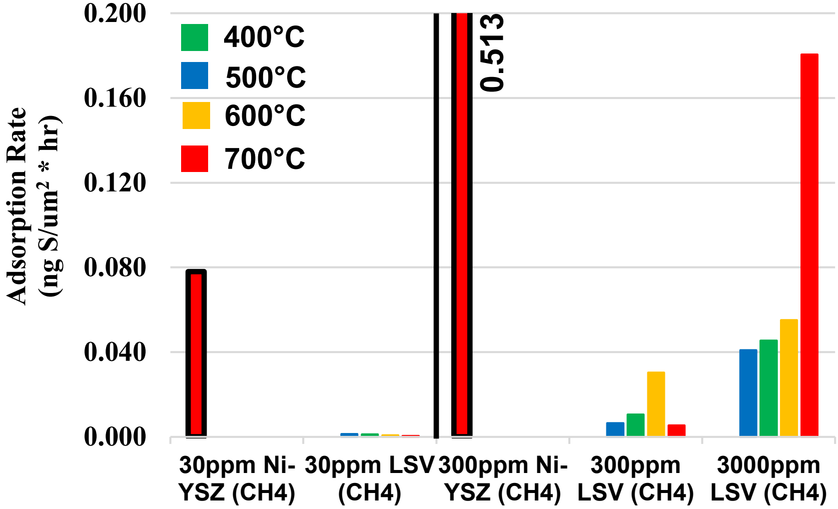
- $LaSrMnO_3$ (LSM)
- $LaSrFeO_3$ (LSF)
- $LaSrCoFeO_3$ (LSFC)
- $LaSrCoO_3$ (LSC)
- $BaSrCoFeO_3$ (BSFC)
- $SmSrCoO_3$ (SSC)
- $LaSrTiO_3$ (LST)
- $LaSrVO_3$ (LSV)

- Perovskites can be used as catalysts for anode and cathode electrodes
  - Potentially be a replacement for Ni-YSZ
- A-site and B-site can be doped with other elements for different effects
- No limit to the fun!!! Some exotic perovskite formulations have 6-7 elements

Motivation – LSV Anode Catalyst Sulfur Tolerance



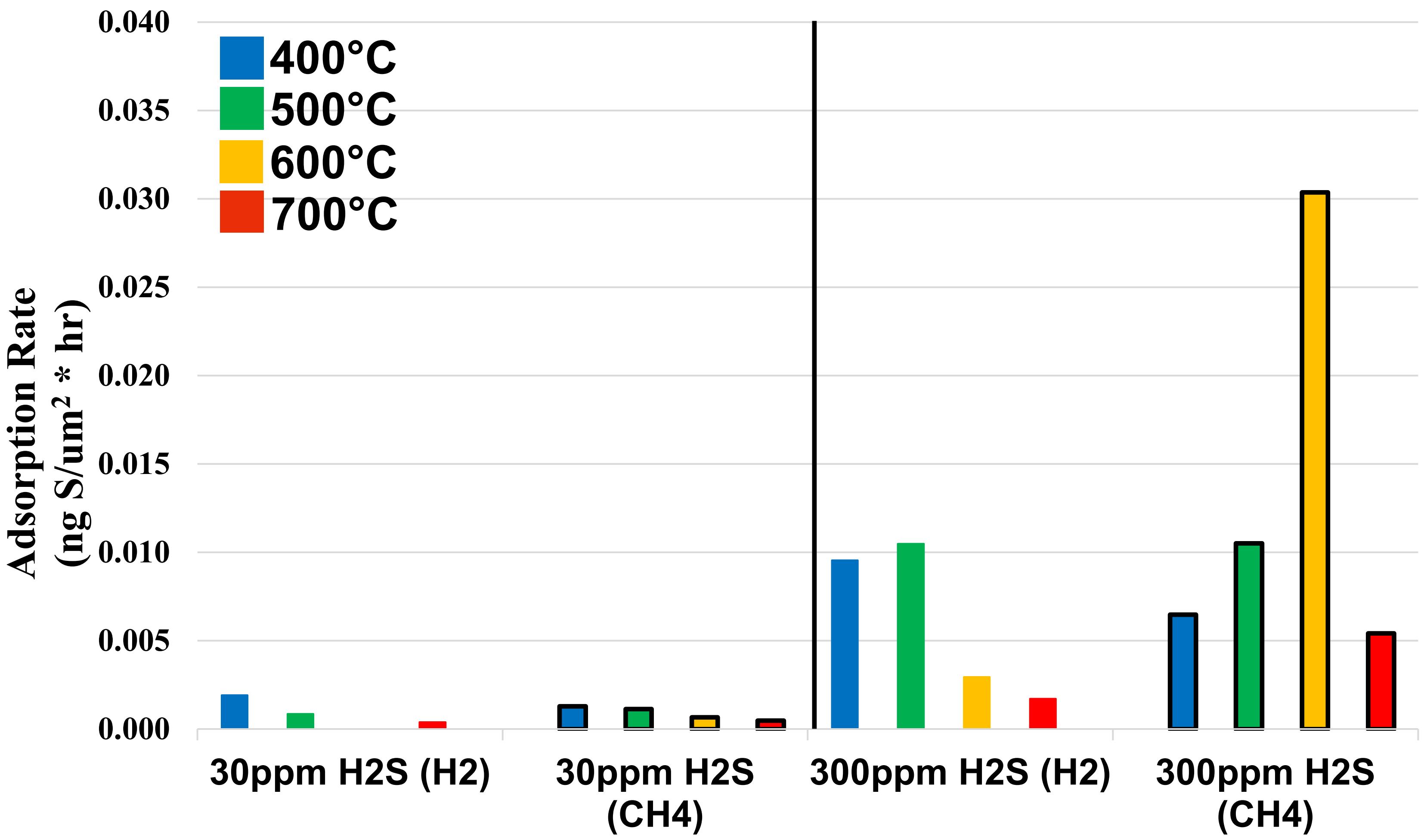




- This study experimentally tests LSV powder:
  - Heated under exposure to C_4H_4S
  - Changed atmosphere to CH_3OH
  - Heated up to 100 hours
  - Sulfur amount characterized using EDS post-experimentation
  - LSV structure characterized using XRD post-experimentation
  - Modeling of C_4H_4S and LSV interaction conducted in parallel
  - Compare adsorption response again previous studies

Aguilar, J. Power Sources, 135, (2004), 17-24

Motivation – Previous ILIR Experimental Testing



- Hydrogen atmosphere testing showed promising results compared to current anode material, Ni-YSZ, even at elevated sulfur concentrations.
- Hydrogen usually produces higher performance in fuel cells (reducing properties/no coking/etc)
  - Methane atmosphere tested to push LSV and see how it responds to light hydrocarbon

Characterization Techniques – SEM, EDS, XRD

SEM – Scanning Electron Microscopy

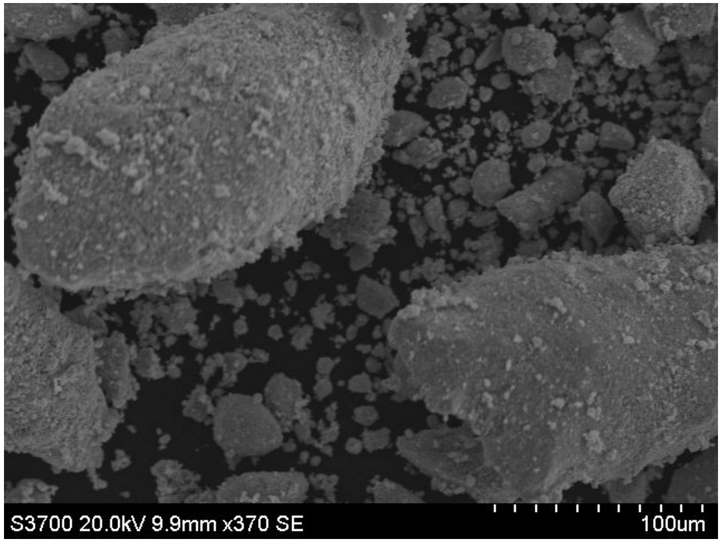
- Calculate average LSV surface area
  - Calculate average LSV H_2S adsorption rate

EDS – Energy Dispersive Spectroscopy

- Determine average LSV sulfur amount
  - Calculate average LSV H_2S adsorption rate

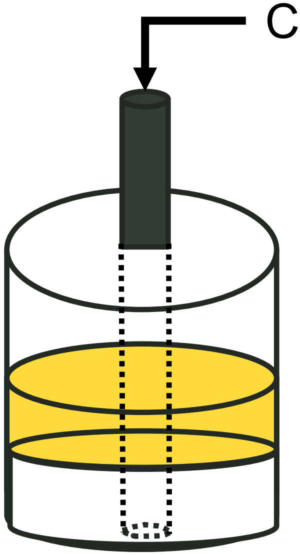
XRD – X-ray Diffraction

- Determine LSV structure
- Determine LSV oxygen content



Experimental Setup – Sample Testing Preparation

LSV

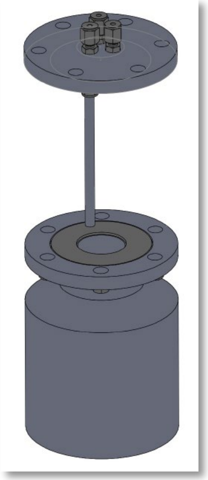


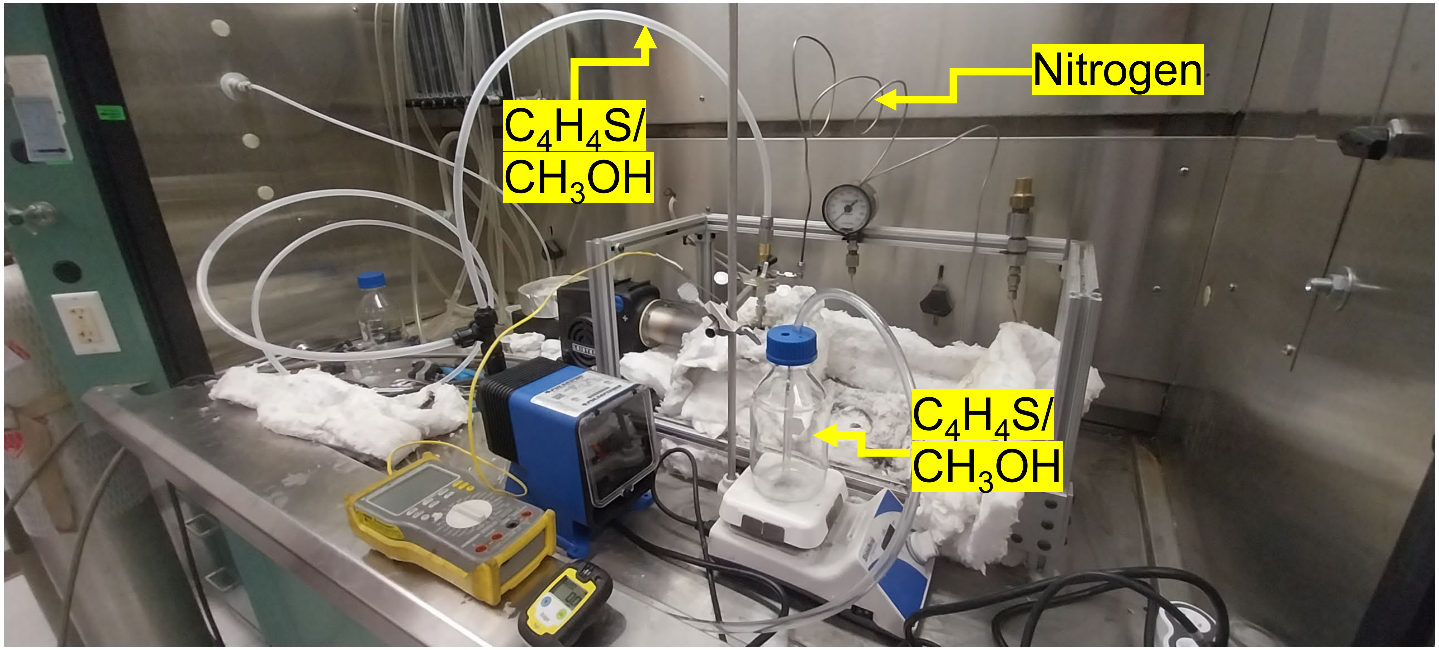
C_4H_4S and Nitrogen

Insulation

LSV Powder

Insulation





Experimental Results – Operating Parameters

N_2 Gas Pressure = 45 PSI

CH_3OH/C_4H_4S Flow Rate = 300 mL/min

C_4H_4S Concentration (ppm)	C_4H_4S/CH_3OH Solution Stirring RPM	**Temperature (C)**	**Time (hours)**
30	500	400	NA
30	500	500	NA
30	500	600	NA
30	500	700	NA
300	500	400	25-100 hours
300	500	500	25-100 hours
300	500	600	25-100 hours
300	500	700	25-100 hours
3000	500	400	10-30 hours
3000	500	500	10-30 hours
3000	500	600	10-30 hours
3000	500	700	10-30 hours

Experimental Results – Adsorption Rate Calculation

$$R_{ads} = \frac{Mass_{sulf,norm}}{\mathrm{Time}_{duration}}$$

$$\downarrow$$

$$Mass_{sulf,norm} = \frac{Mass_{sulf}}{SA}$$

$$Time_{duration} = Gas\ Exposure\ Time\ (hrs)$$

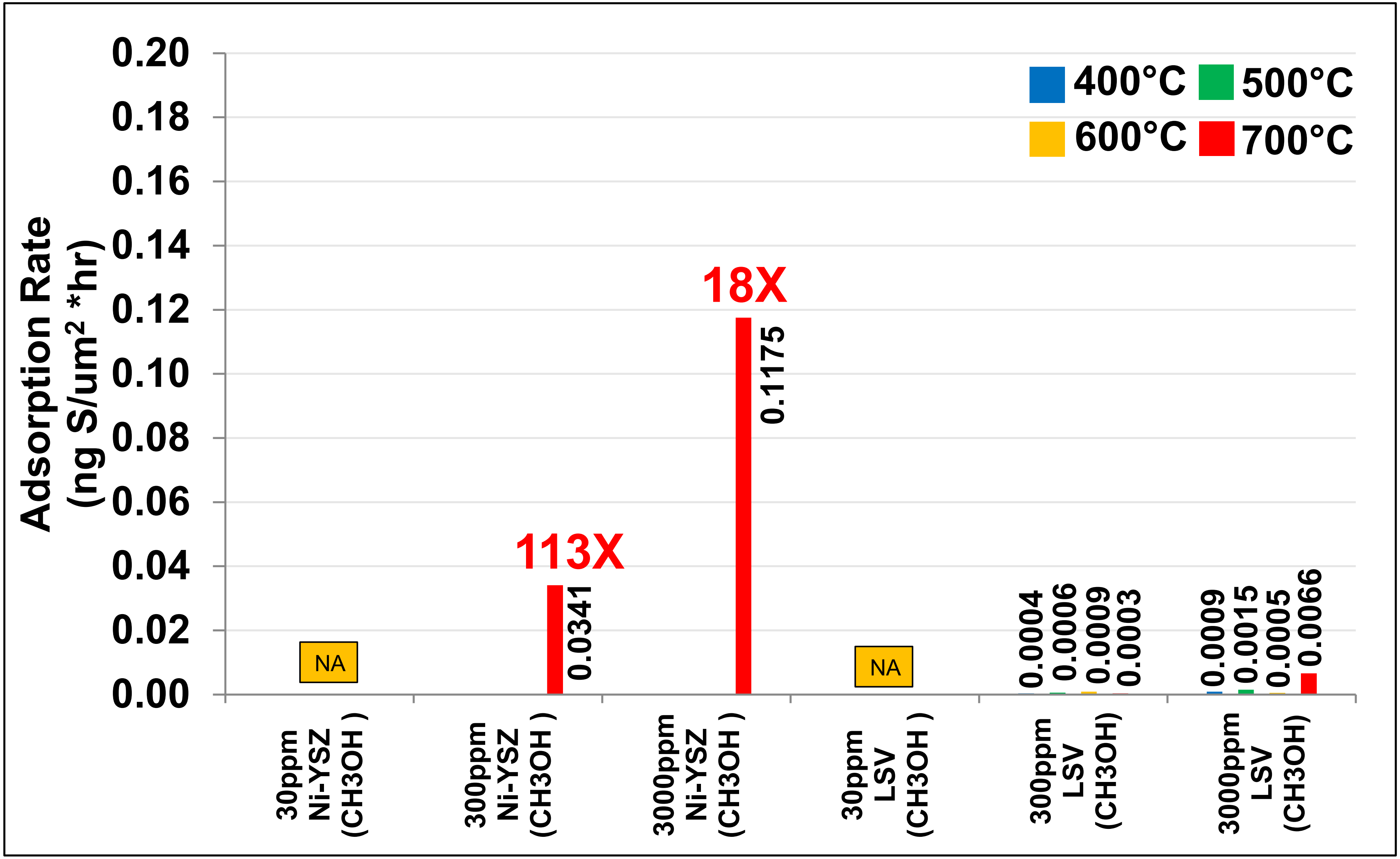
$$\downarrow$$

$$Mass_{sulf} = Sulfur\ Mass\ (ng) \longleftarrow \textbf{EDS}$$

$$\textbf{SA} = Surface\ Area\ (\mu m^2) \longleftarrow \textbf{SEM}$$

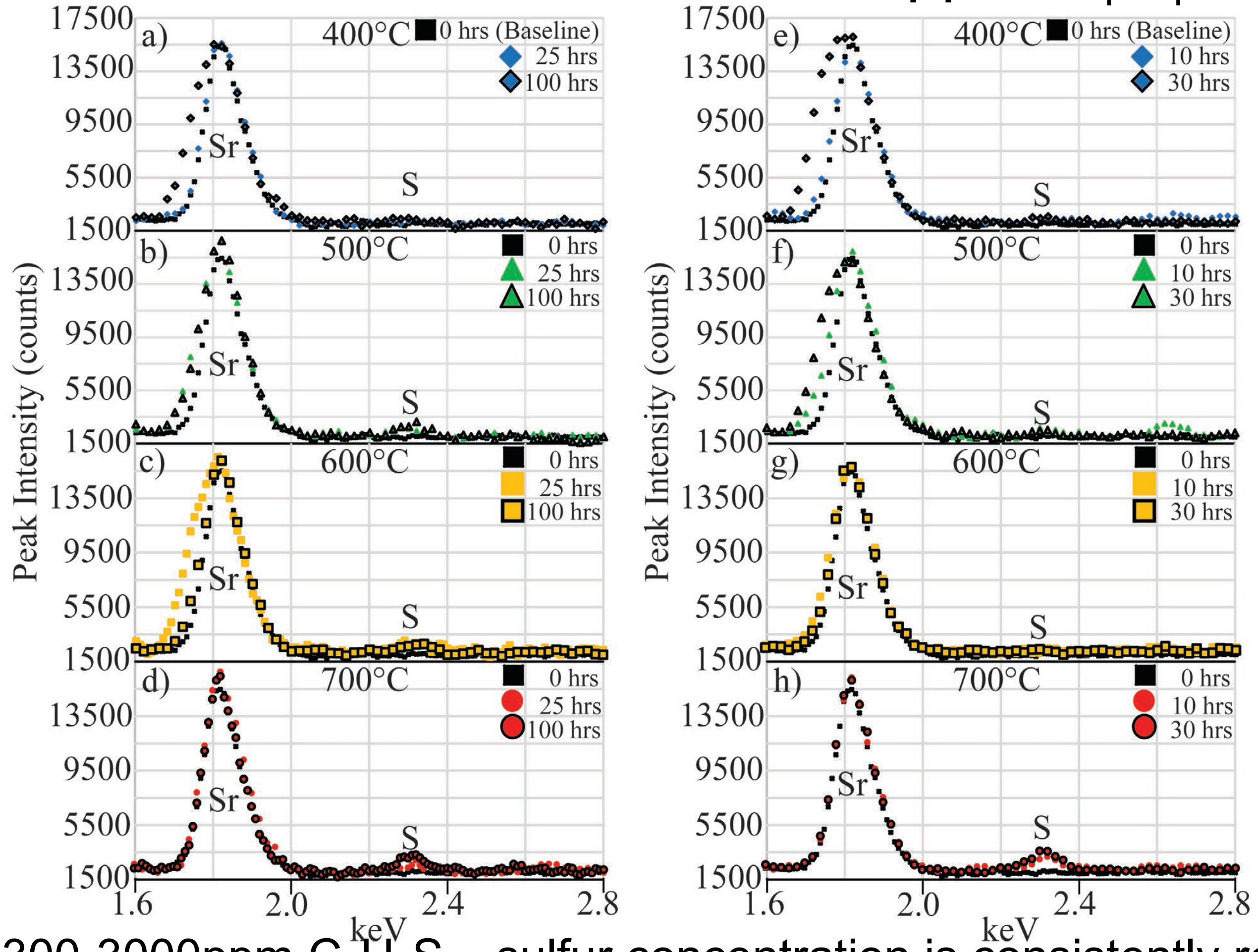
- EDS Provides Weight % Sulfur - Convert to Sulfur Mass
- SEM Provides Agglomerate Size - Determine Surface Area

Experimental Results – CH_3OH Adsorption Rate Results



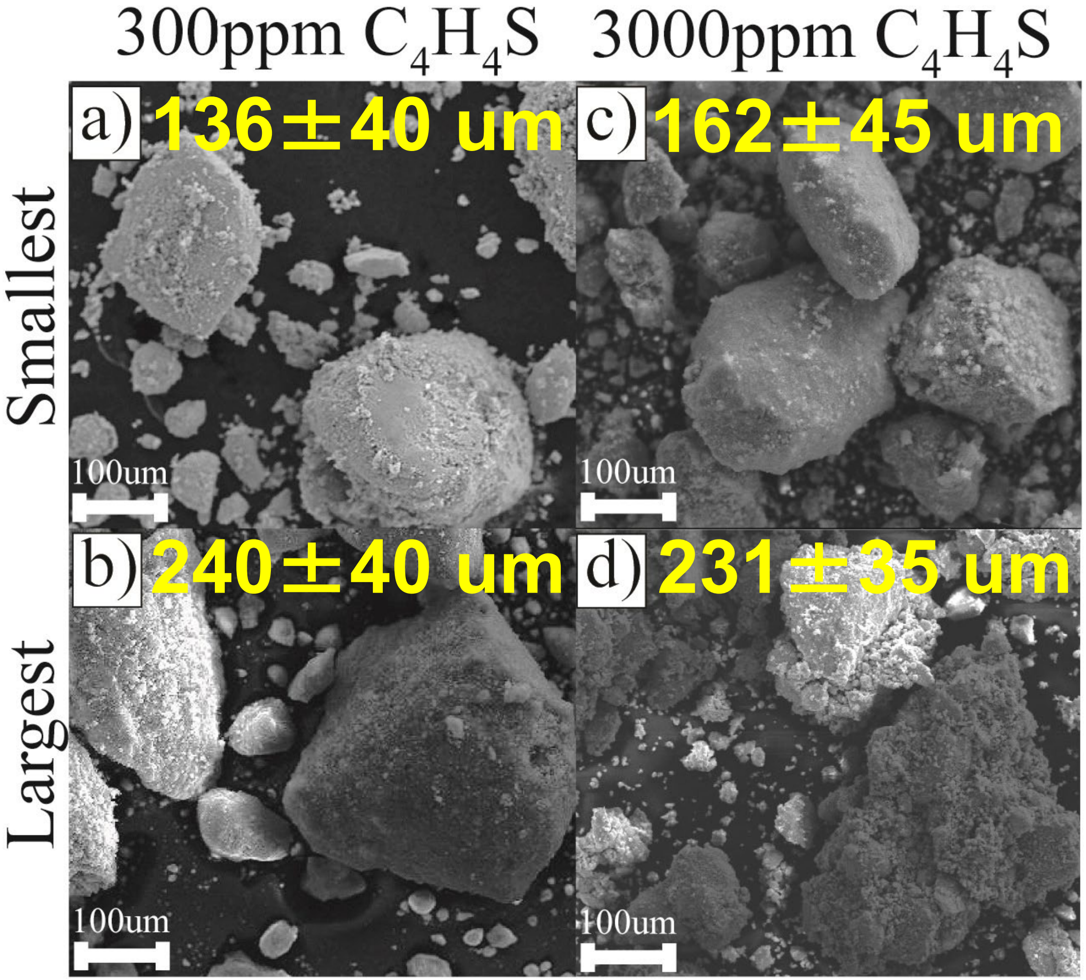
Experimental Results – EDS CH_3OH Results

300ppm C_4H_4S 3000ppm C_4H_4S



- 300-3000ppm C_4H_4S – sulfur concentration is consistently reduced regardless of time
  - Slight increase in sulfur concentration at 700C
  - Hypothesis for reduced sulfur overall and increased sulfur at 700C is thought to be from methanol contribution

Experimental Results – SEM CH_3OH Results



- Overall agglomerate shape is non-uniform
- LSV agglomerate size appears to stay constant with increasing C_4H_4S concentration

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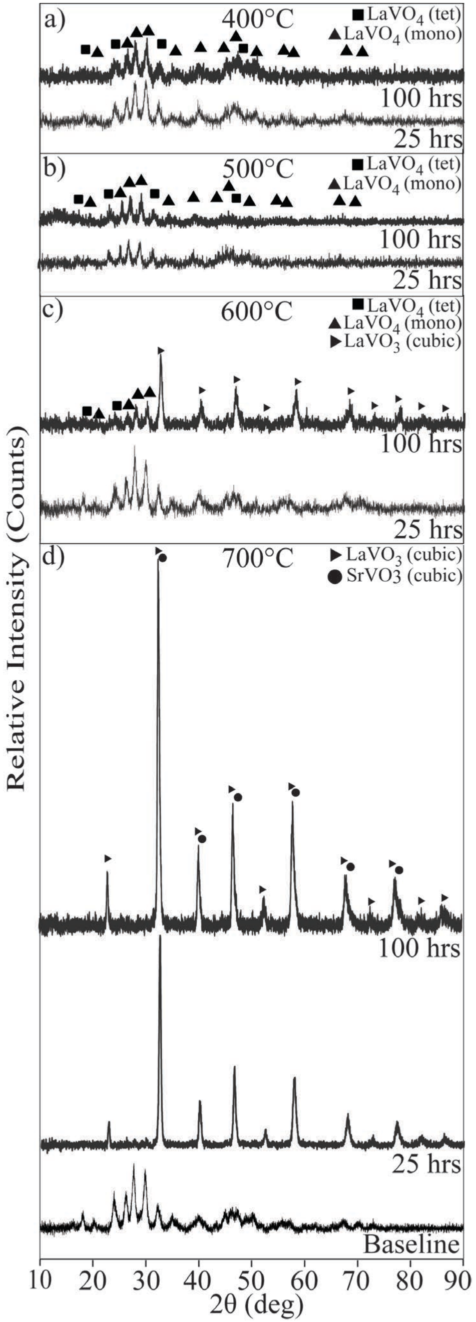
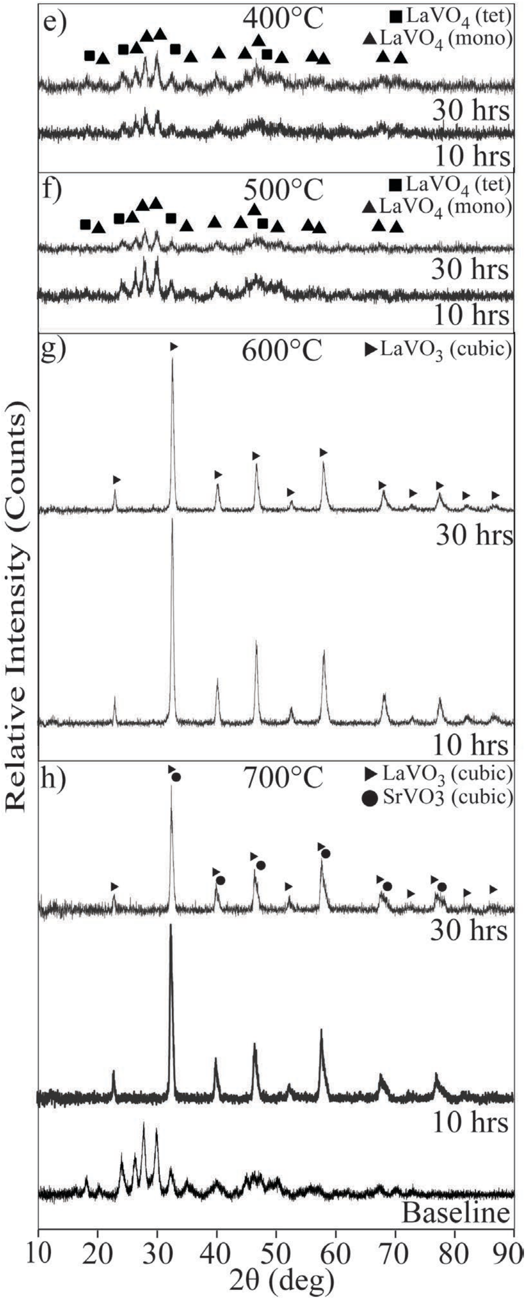
Experimental Results – 300ppm C_4H_4S CH_3OH XRD Results



- LSV stays relatively consistent in peaks height between 400-600C.
  - Large peak increase at 700C
- LSV is transitioning between cubic and monoclinic/tetragonal at 600C.
  - All three phases present at 300ppm C_4H_4S
- LSV crystal structure changes:
  - 400C – Monoclinic/Tetragonal
  - 500C – Monoclinic/Tetragonal
  - 600C – Cubic/Monoclinic/Tetragonal
  - 700C – Cubic

Experimental Results – 3000ppm C_4H_4S CH_3OH XRD Results



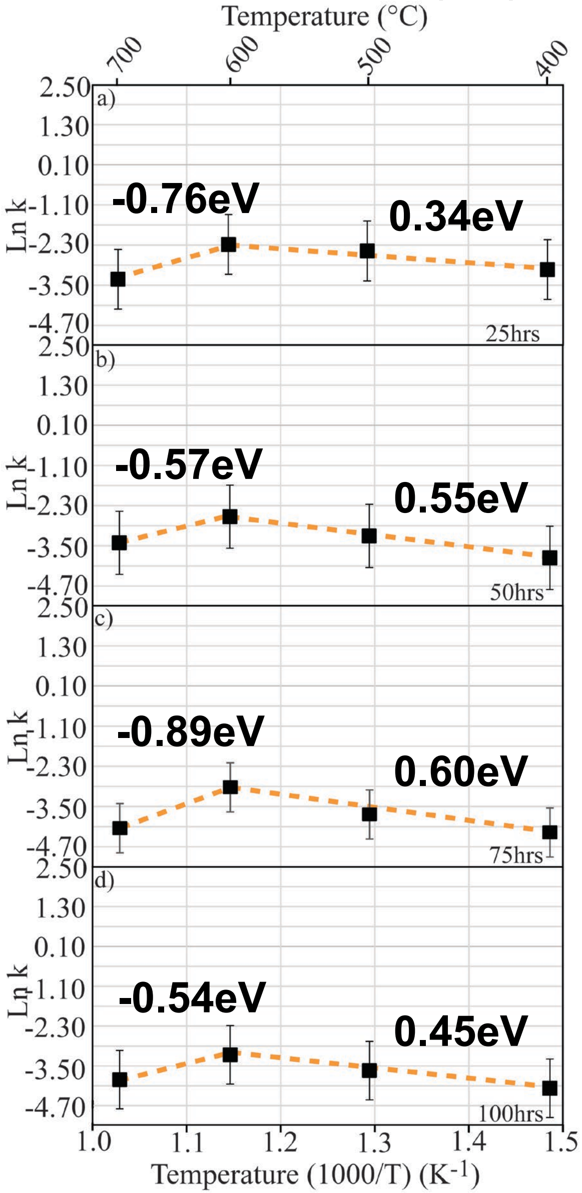
- LSV stays relatively consistent in peaks height between 400-600C.
  - Large peak increase between 600-700C

- LSV is transitioning between cubic and monoclinic/tetragonal at 600C.
  - Only cubic phase present at 3000ppm C_4H_4S
  - Could be the result of C_4H_4S concentration

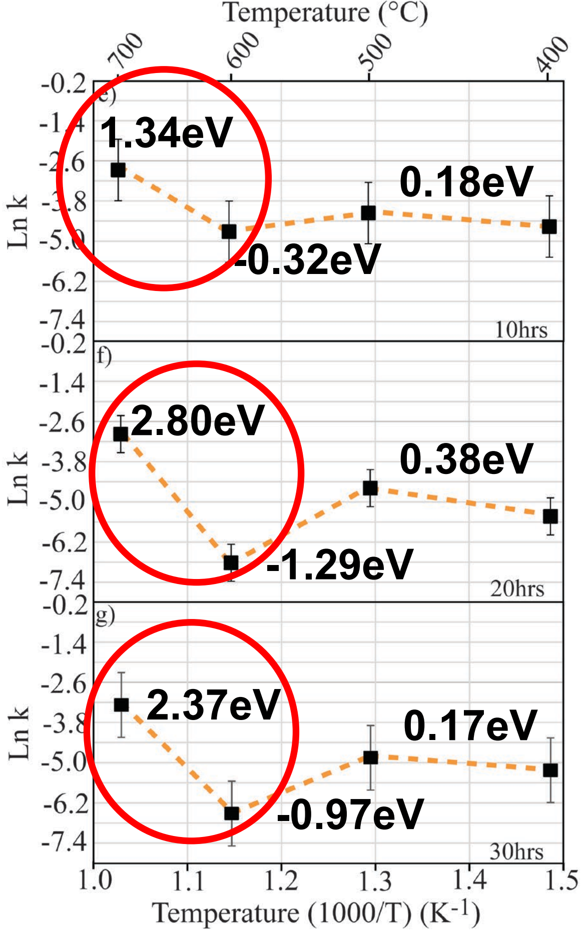
- LSV crystal structure changes:
  - 400C – Monoclinic/Tetragonal
  - 500C – Monoclinic/Tetragonal
  - 600C – Cubic
  - 700C – Cubic

Experimental Results – CH_3OH Activation Energy Results

300ppm C_4H_4S



3000ppm C_4H_4S



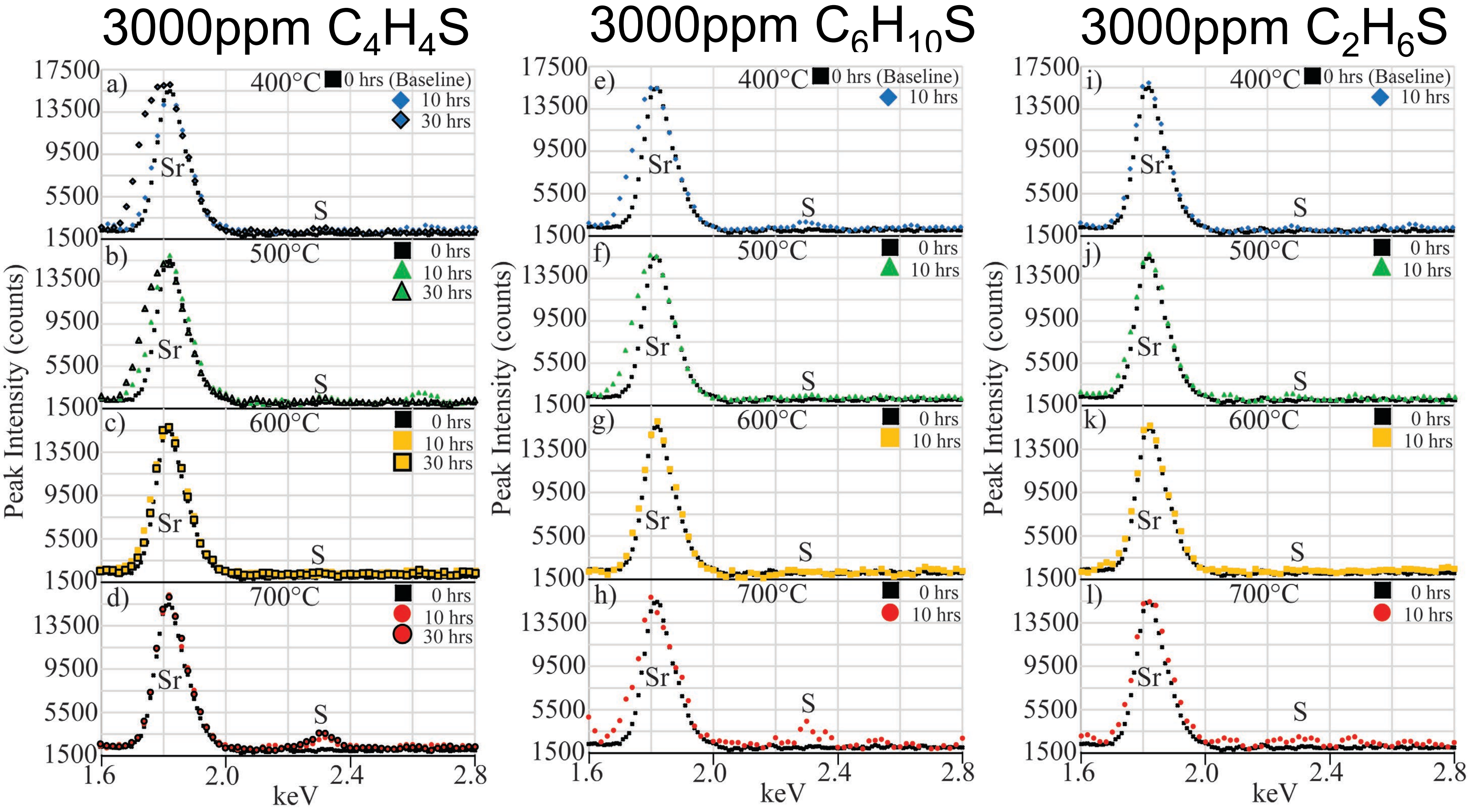
Experimental Results – CH_3OH Activation Energy Results (cont.)

- Activation energies for 300ppm and 3000ppm C_4H_4S samples are generally statistically similar over their respective heating durations. Generally, much lower than Ni-YSZ.

- Two activation energies for most of the samples
  - A third activation energy emerges for the 3000ppm C_4H_4S samples from 600-700C
  - Third activation energy is a large positive value which supports the increased sulfur adsorption observed

- The increase in sulfur content at 700C and overall increased sulfur tolerance:
  - Methanol has a greater affinity to LSVs reaction sites than sulfur.
  - Methanol starts to thermally decompose at 650C
  - This hypothesis will be explored over the next few slides
    - Tested two additional sulfur compounds in methanol for increased sulfur at 700C
    - 3000ppm Diallyl sulfide ($C_6H_{10}S$), Dimethyl sulfide (C_2H_6S)

Experimental Results – $C_6H_{10}S$ and C_2H_6S EDS Comparison Results



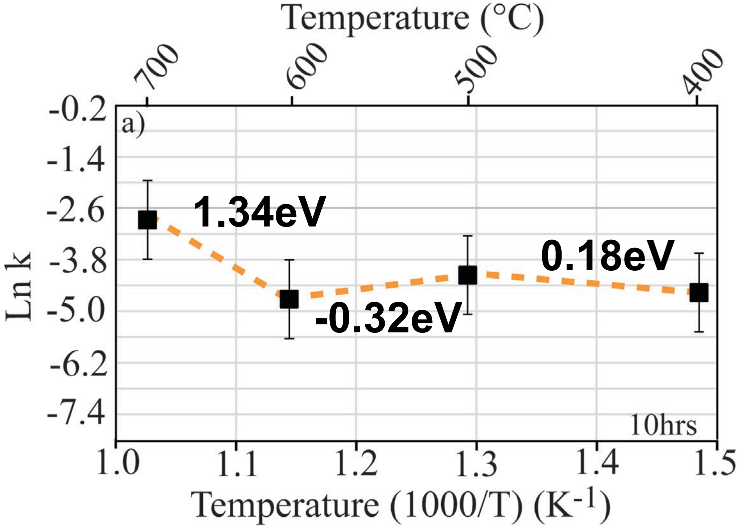
3000ppm C_4H_4S

3000ppm $C_6H_{10}S$

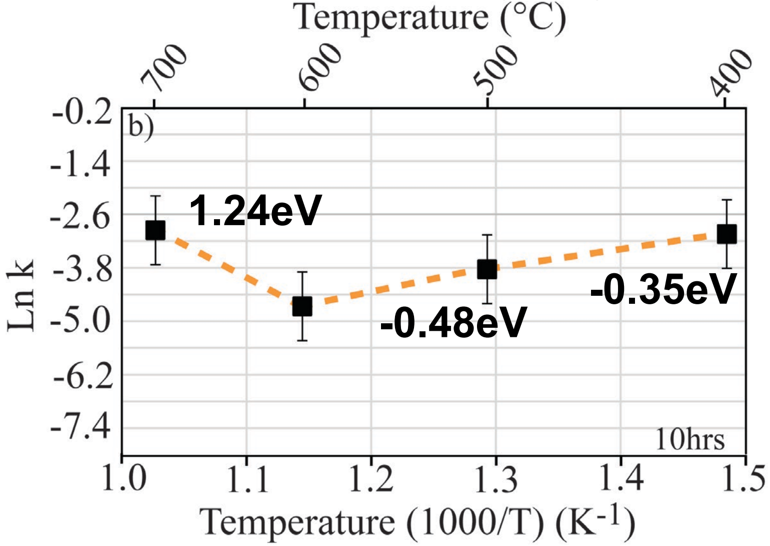
3000ppm C_2H_6S

Experimental Results – $C_6H_{10}S$ and C_2H_6S Comparison Activation Energy Results

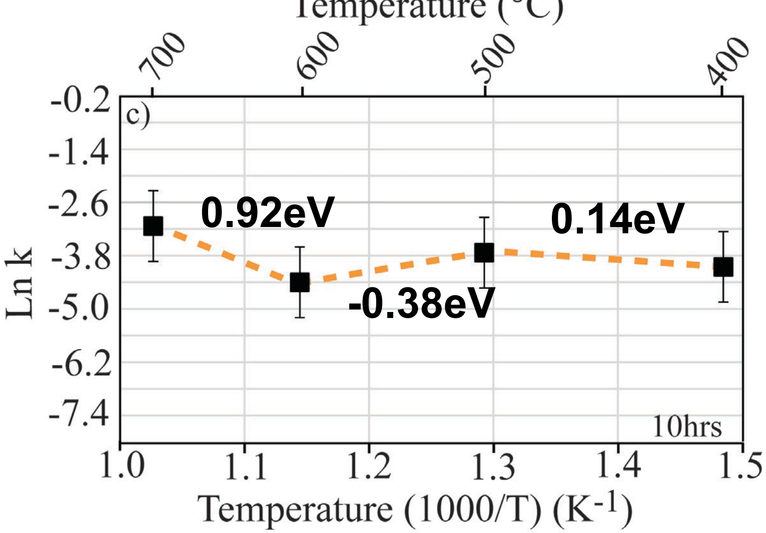
3000ppm C_4H_4S



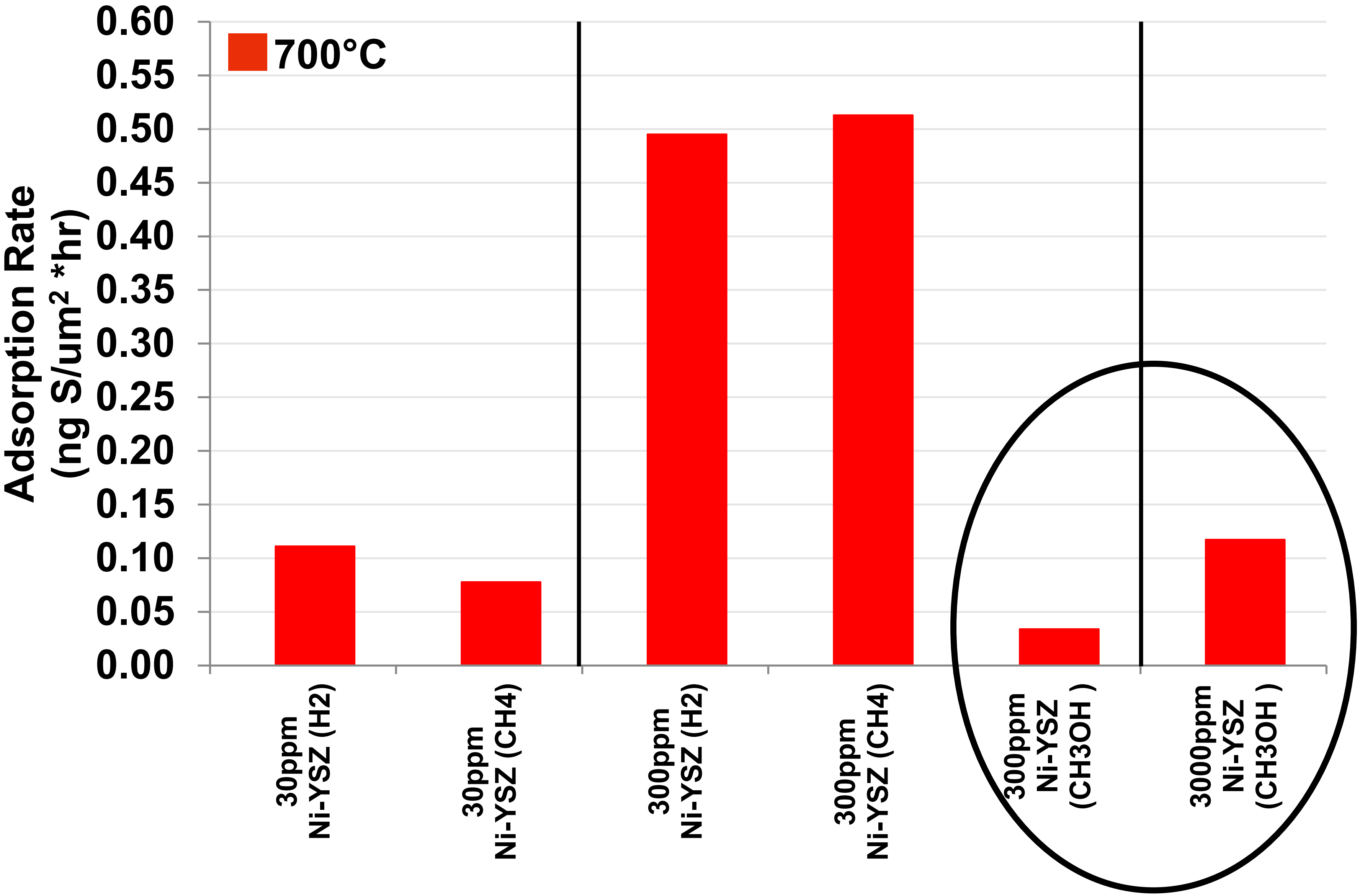
3000ppm $C_6H_{10}S$



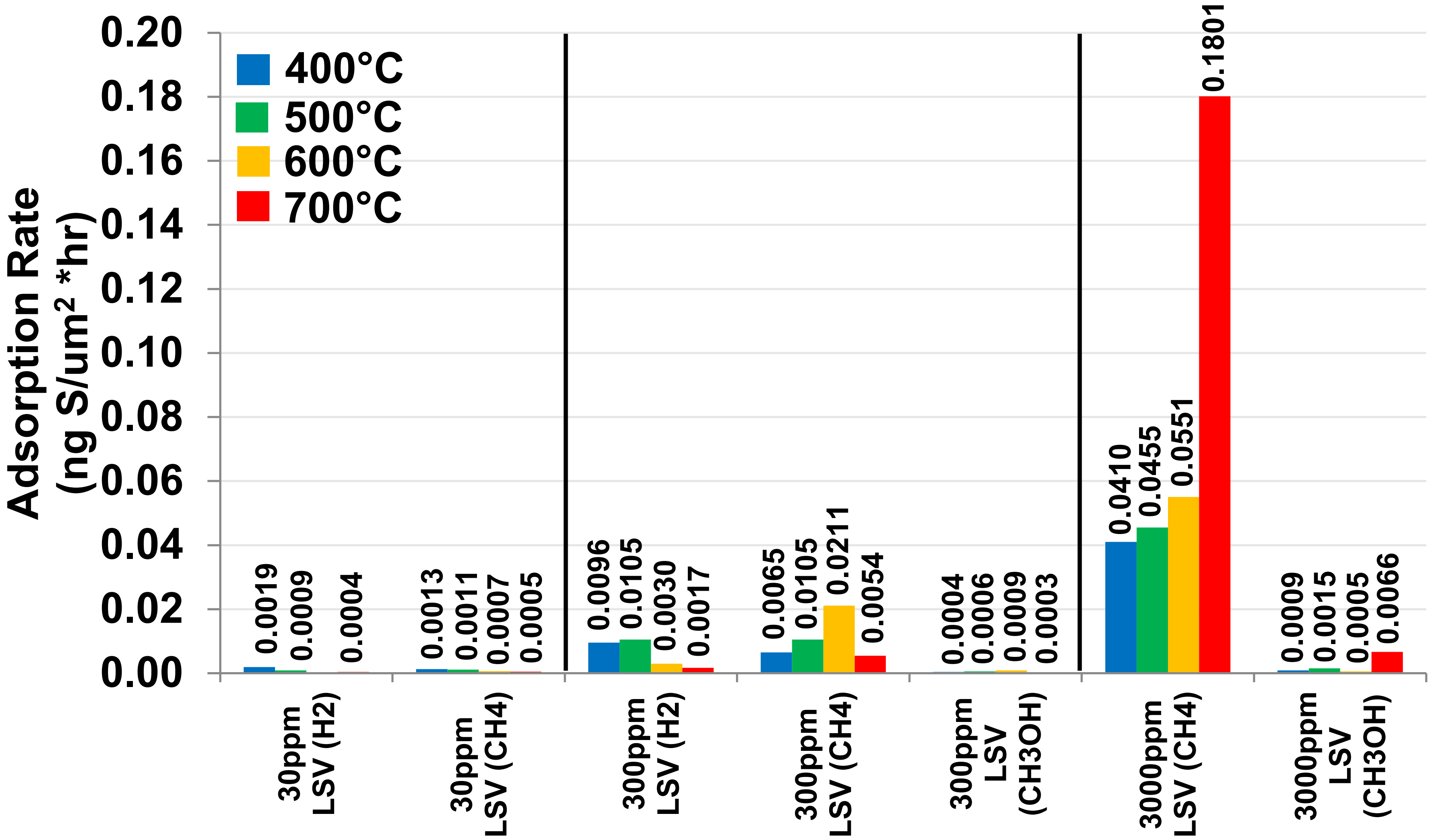
3000ppm C_2H_6S



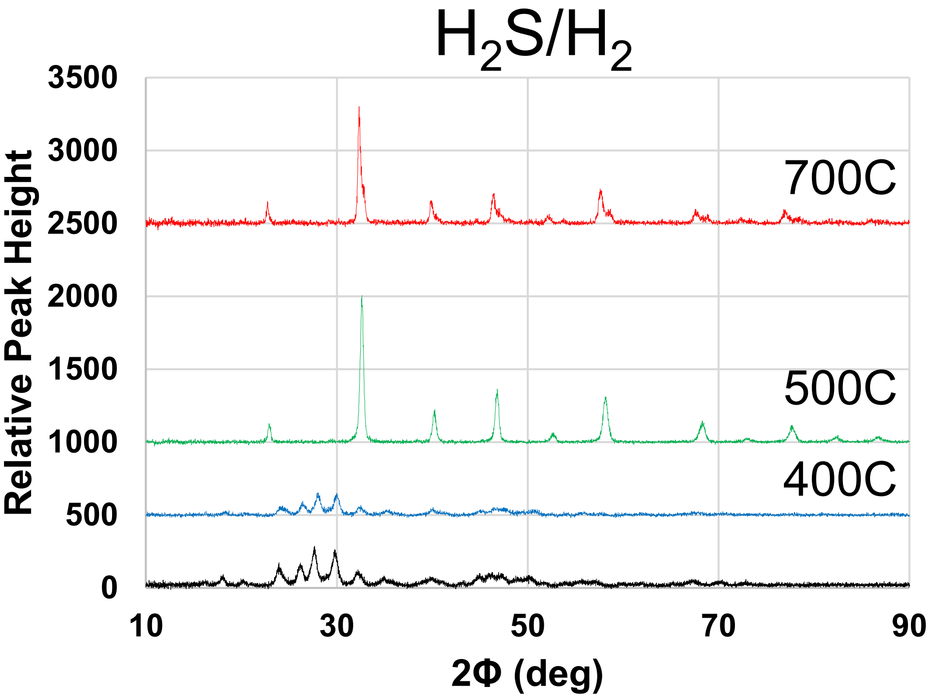
Experimental Results – Ni-YSZ Adsorption Rate Comparison with Previous Results

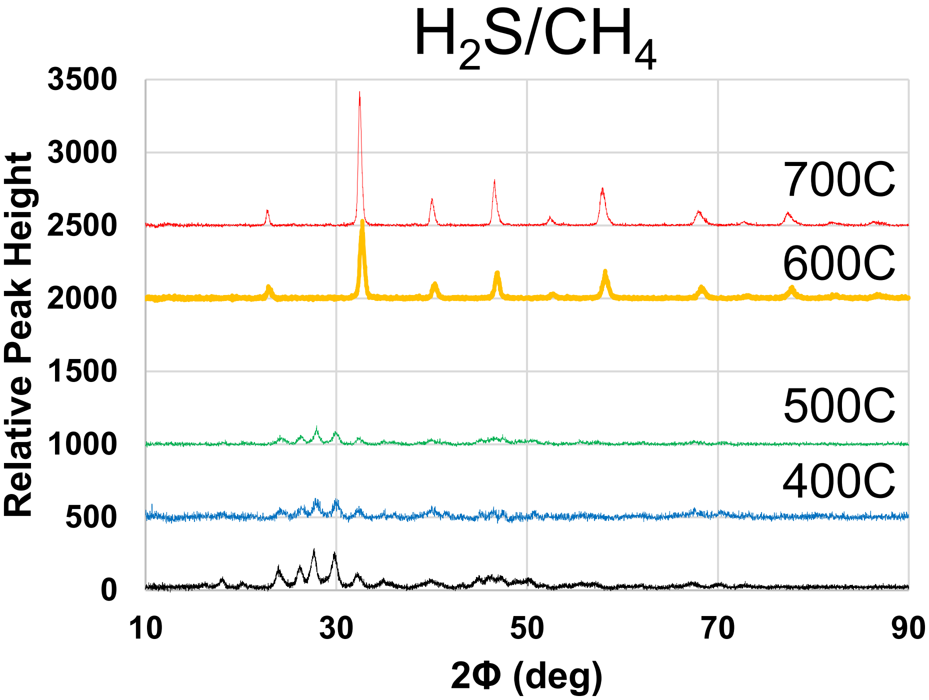


Experimental Results – LSV Adsorption Rate Comparison with Previous Results



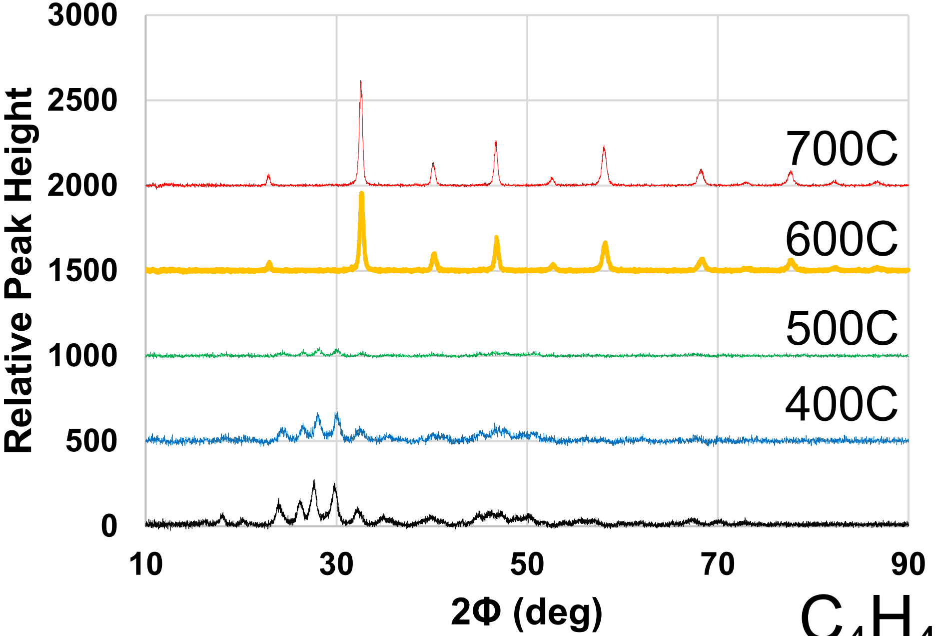
Experimental Results – 30ppm H_2S XRD Comparison with Previous Results



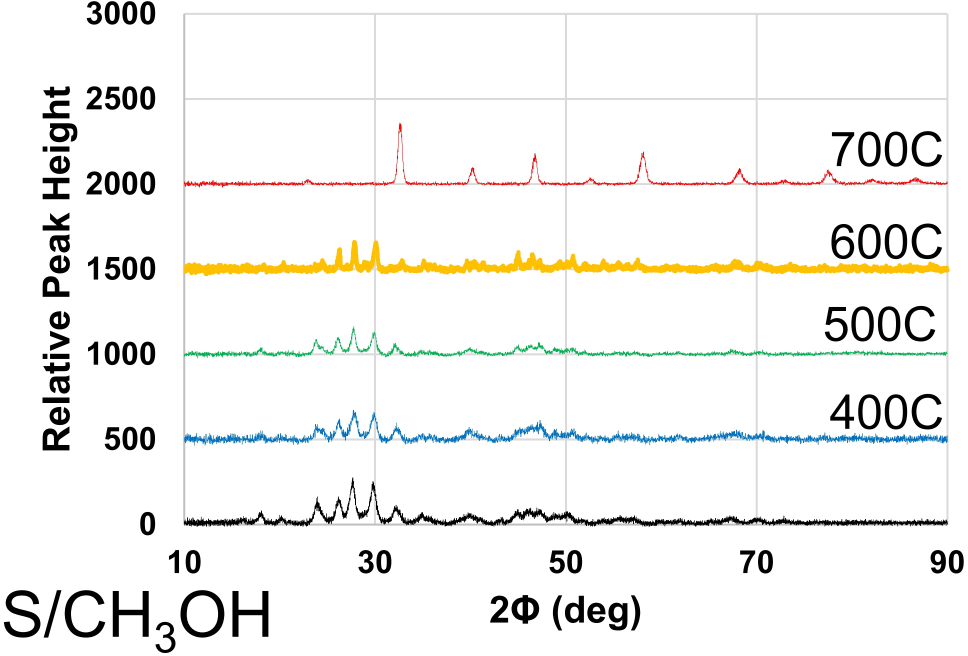


Experimental Results – 300ppm H_2S/C_4H_4S XRD Comparison with Previous Results

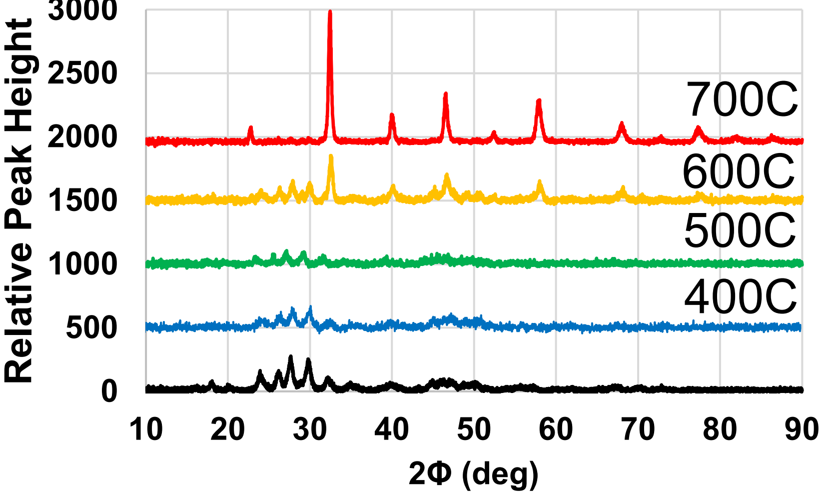
H_2S/H_2



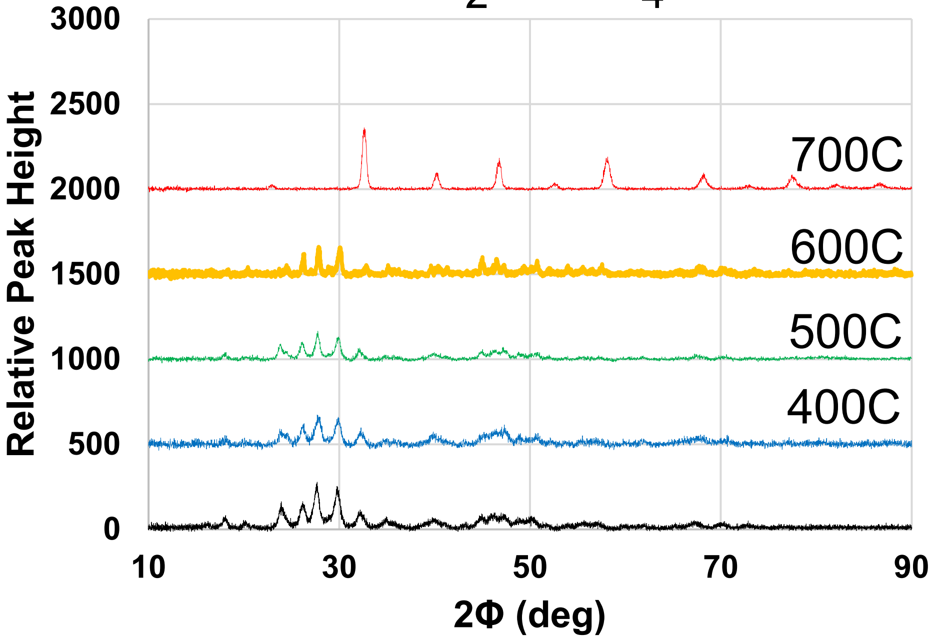
H_2S/CH_4



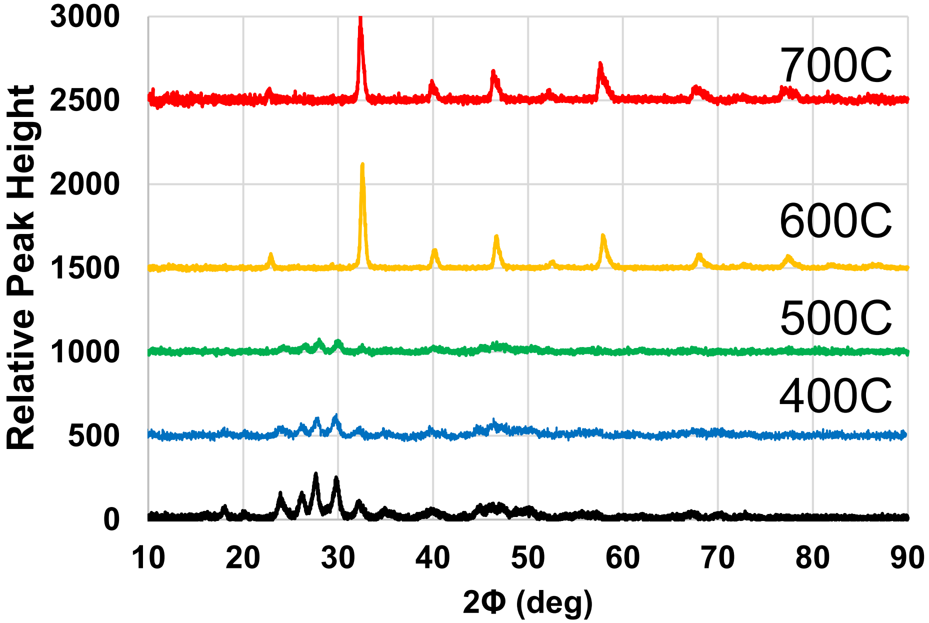
C_4H_4S/CH_3OH



Experimental Results – 3000ppm H_2S/C_4H_4S XRD Comparison with Previous Results



H_2S/CH_4

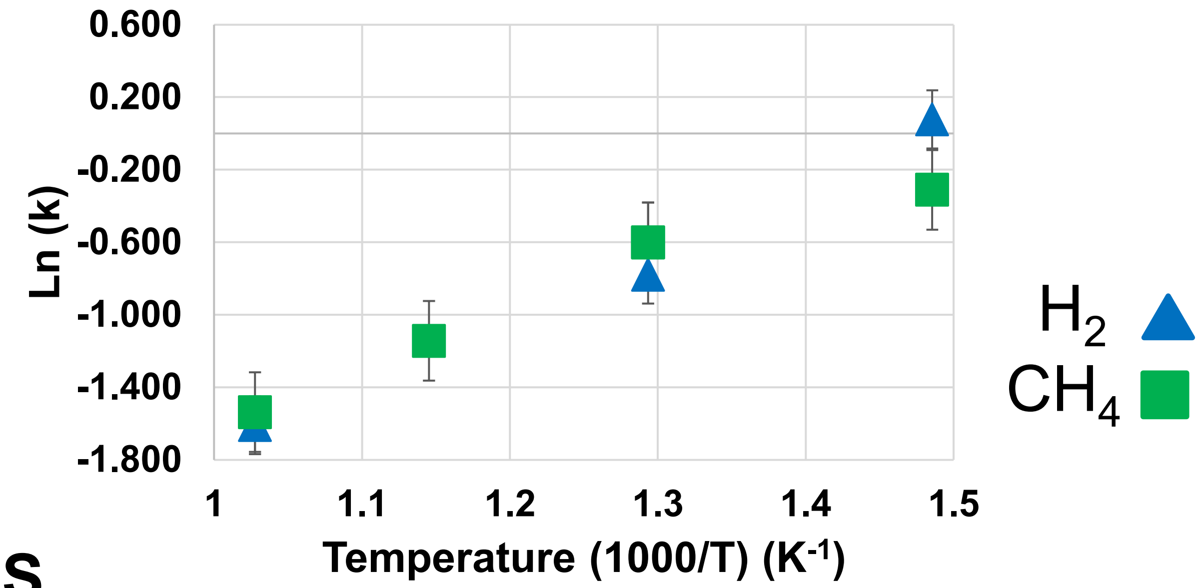


C_4H_4S/CH_3OH

Experimental Results – Activation Energy Comparison with Previous Results

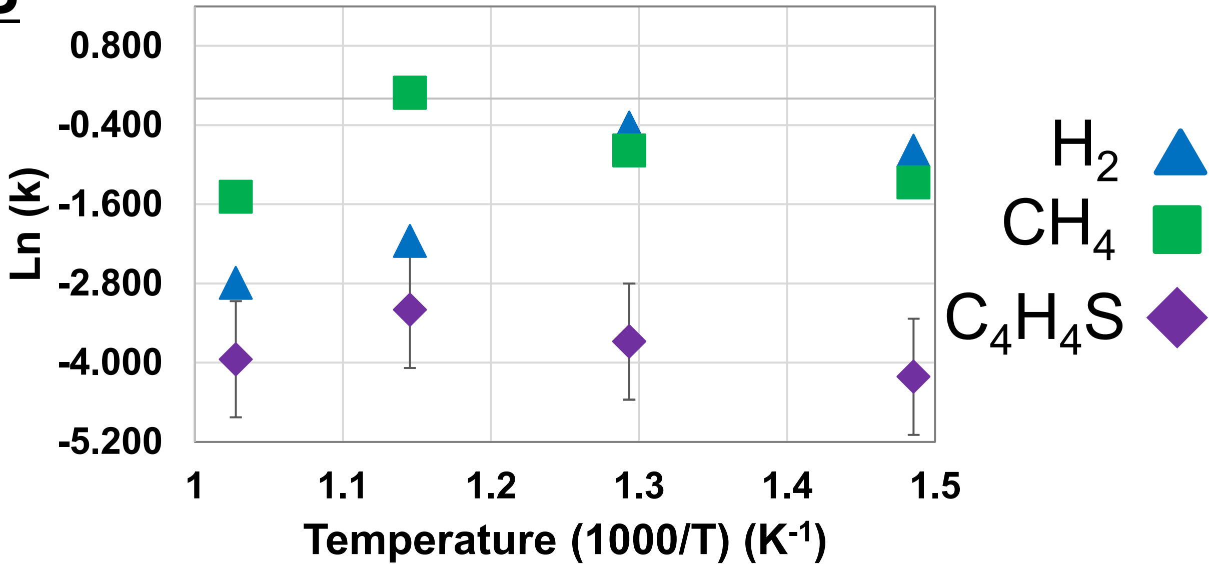
30ppm H_2S

- Reduced CH_4 adsorption/kinetics at low temperature results from CS_2 formation
- Overall, very similar to H_2
- CH_3OH not performed due to low adsorption at 300/3000ppm.



300ppm H_2S/C_4H_4S

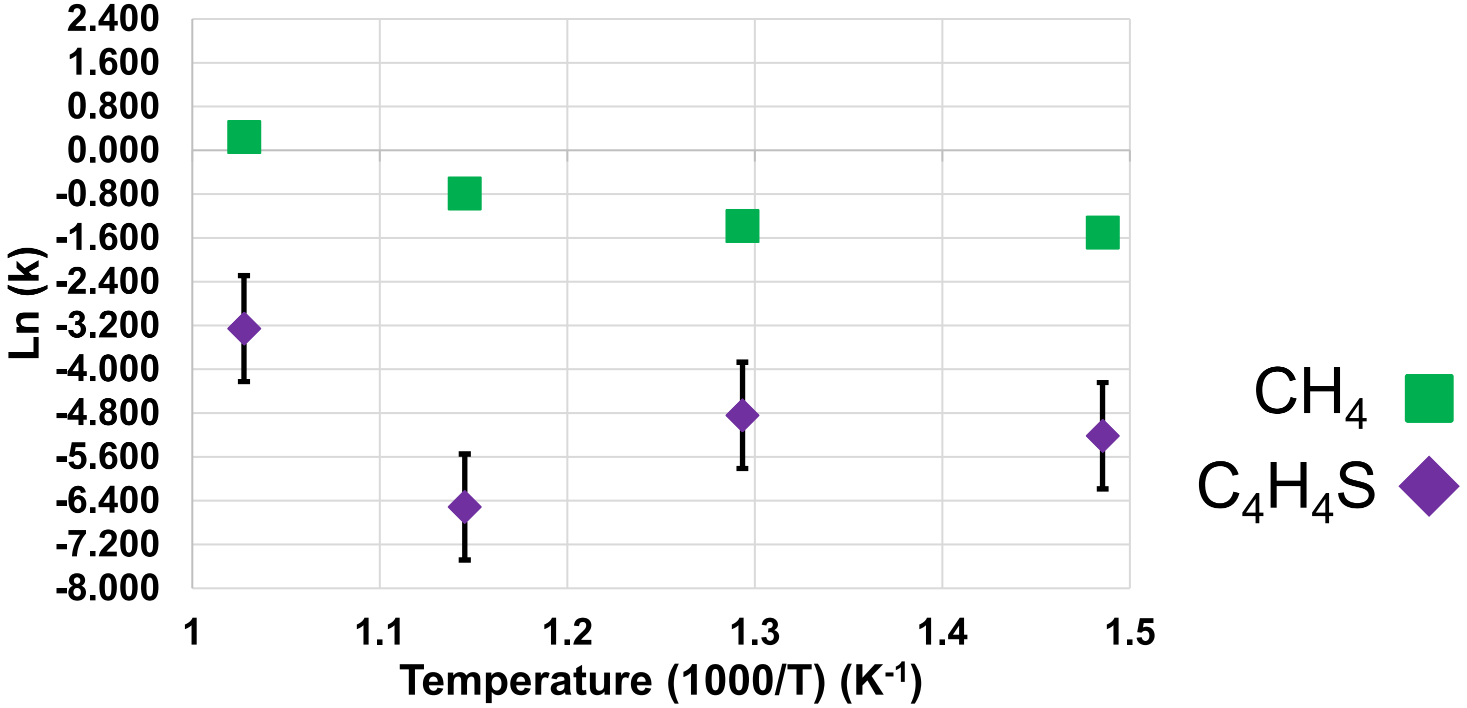
- CH_3OH results considerably lower than both CH_4 and H_2 results, especially at <500C.
- Calculated CH_3OH activation energies support sulfur adsorption results collected.



Experimental Results – Activation Energy Comparison with Previous Results

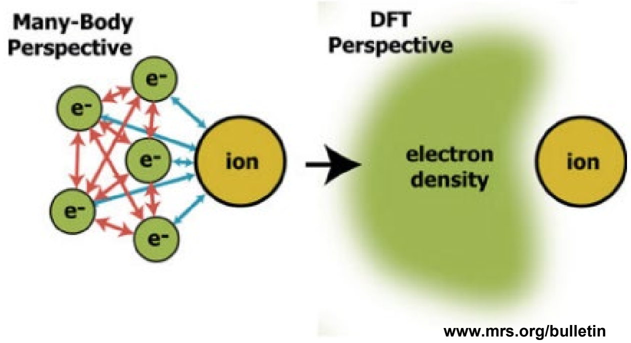
<u>3000ppm H_2S/C_4H_4S</u>

- CH_3OH results considerably lower than CH_4 results for all temperatures.
- Calculated CH_3OH activation energies support sulfur adsorption results collected.
- Very promising results for such an elevated sulfur concentration.



Theoretical Approach to Research Problem

Atomistic Modeling and Simulation



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Density Functional Theory in Catalysis

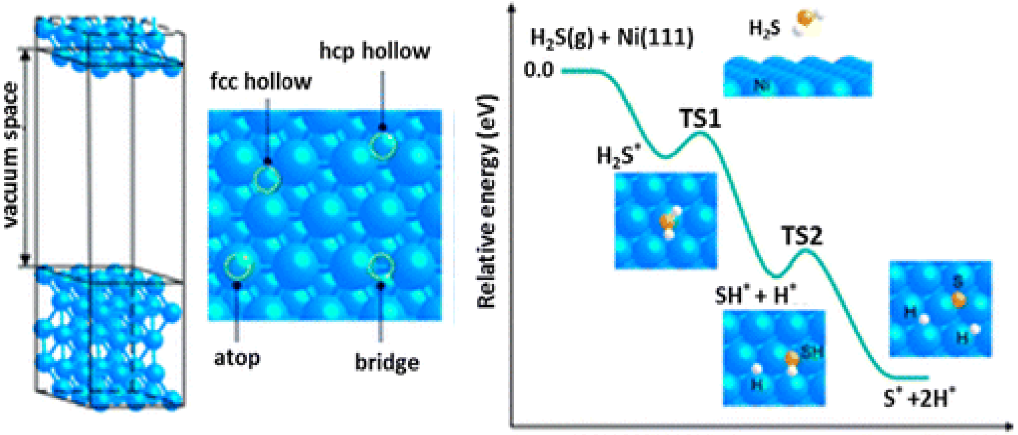
- Atomic structures and surfaces
- Active sites and chemical states
- Adsorption and diffusion
- Electronic structure and distribution

Density Functional Theory Literature Ni/YSZ

- Adsorption of H_2S on nickel surfaces
- Two-step dissociative adsorption reaction
- Favorable reaction process

Density Functional Theory LSV Treatment

- VASP:DFT:GGA:PBEsol+U:520



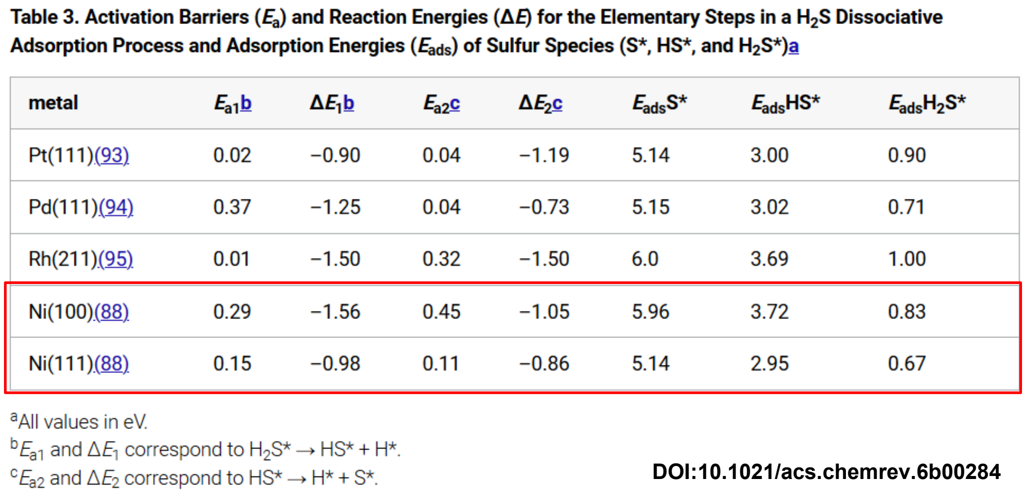


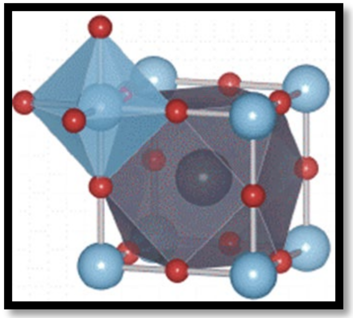
Table 3. Activation Barriers (E_a) and Reaction Energies (ΔE) for the Elementary Steps in a H_2S Dissociative Adsorption Process and Adsorption Energies (E_{ads}) of Sulfur Species (S*, HS*, and H$_2$S*)[a]

metal	E_{a1}[b]	ΔE_1[b]	E_{a2}[c]	ΔE_2[c]	E_{ads}S*	E_{ads}HS*	E_{ads}H$_2$S*
Pt(111)(93)	0.02	−0.90	0.04	−1.19	5.14	3.00	0.90
Pd(111)(94)	0.37	−1.25	0.04	−0.73	5.15	3.02	0.71
Rh(211)(95)	0.01	−1.50	0.32	−1.50	6.0	3.69	1.00
Ni(100)(88)	0.29	−1.56	0.45	−1.05	5.96	3.72	0.83
Ni(111)(88)	0.15	−0.98	0.11	−0.86	5.14	2.95	0.67

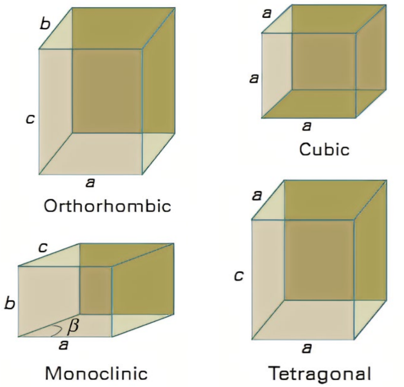
[a] All values in eV.
[b] E_{a1} and ΔE_1 correspond to $H_2S^* \rightarrow HS^* + H^*$.
[c] E_{a2} and ΔE_2 correspond to $HS^* \rightarrow H^* + S^*$.

DOI:10.1021/acs.chemrev.6b00284

Theoretical Details



DOI:10.1103/PhysRevB.89.134103



Lanthanum Vanadate ($LaVO_3$) - Reduced

- Orthorhombic: stable (Pnma)
  - a = 5.677 Å, b = 7.942 Å, c = 5.591 Å
  - α = 90.053°, β = 90.115°, γ = 90.003°
- Cubic: metastable ($Pm\bar{3}m$)
  - a = 3.950 Å, b = 3.950 Å, c = 3.950 Å
  - α = 90.000°, β = 90.000°, γ = 90.000°
  - Decomposes to orthorhombic

Lanthanum Orthovanadate ($LaVO_4$) - Oxidized

- Tetragonal: stable ($I4_1/amd$)
  - a = 6.268 Å, b = 6.268 Å, c = 6.268 Å
  - α = 106.091°, β = 106.091°, γ = 116.466°
- Monoclinic: metastable ($P2_1/c$)
  - a = 7.353 Å, b = 6.804 Å, c = 8.463 Å
  - α = 54.455°, β = 90.000°, γ = 90.000°
  - Decomposes to tetragonal

Lanthanum Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) - Mixed

Hydrogen

Temperature (C)	[H2S] (ppm)	Facet 1	Phase	Facet 2	Phase	Facet 3	Phase
400	30	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**		
600	30						
700	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**		
400	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
700	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**

Methane

Temperature (C)	[H2S] (ppm)	Facet 1	Phase	Facet 2	Phase	Facet 3	Phase
400	30	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	30	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
700	**30**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
400	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic	**(2,1,1)**	**Cubic**
700	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**

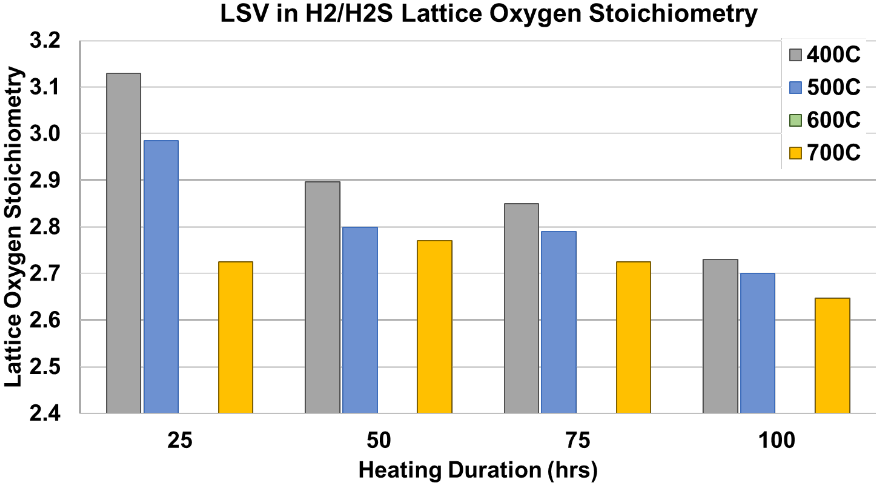
Methanol

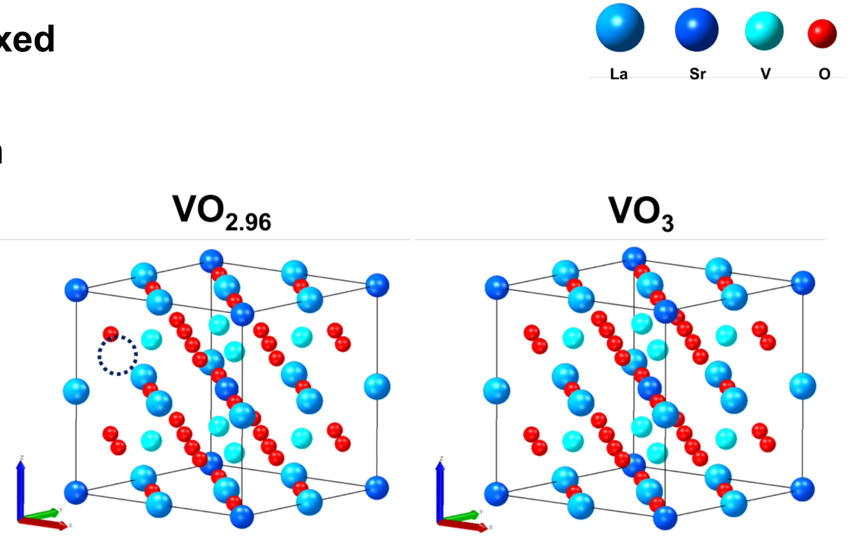
Temperature (C)	[H2S] (ppm)	Facet 1	Phase	Facet 2	Phase	Facet 3	Phase
400	30						
500	30						
600	30						
700	30						
400	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
500	300	(1,2,0)	Monoclinic	(0,1,2)	Monoclinic		
600	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**
700	**300**	**(1,1,0)**	**Cubic**	**(2,0,0)**	**Cubic**	**(2,1,1)**	**Cubic**

Theoretical Details Cont.

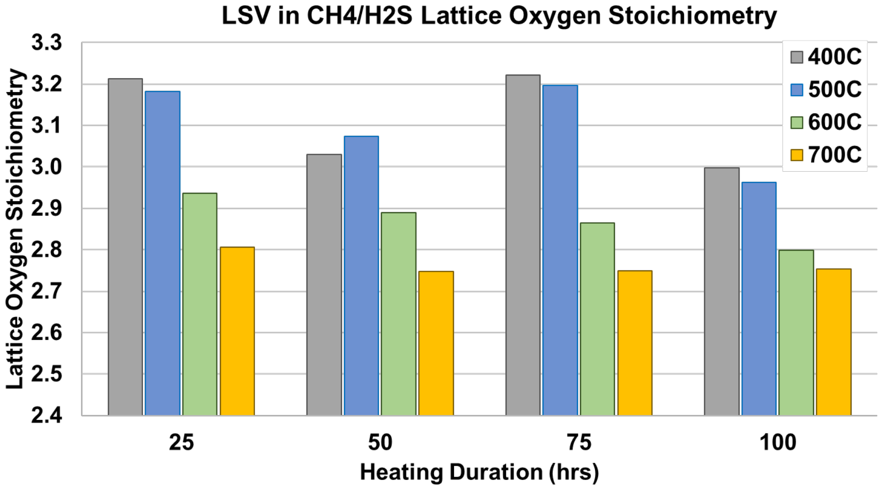
Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Mixed

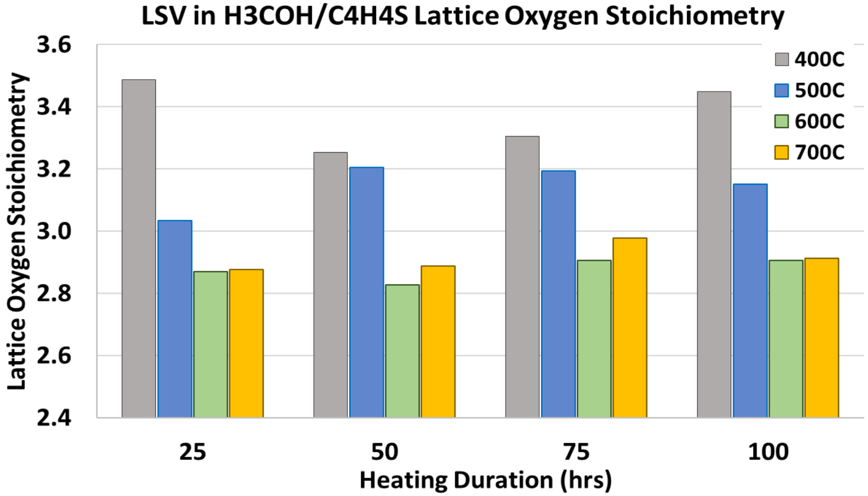
- Gas/temperature dependent oxygen stoichiometry
- Increased sulfur accumulation with increasing oxygen


LSV in H2/H2S Lattice Oxygen Stoichiometry



- Monoclinic → Tetragonal → **Cubic**


LSV in CH4/H2S Lattice Oxygen Stoichiometry


LSV in H3COH/C4H4S Lattice Oxygen Stoichiometry

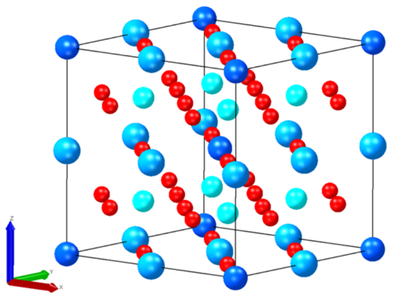
Theoretical Details Cont.

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110}, {211} Facets

La Sr V O

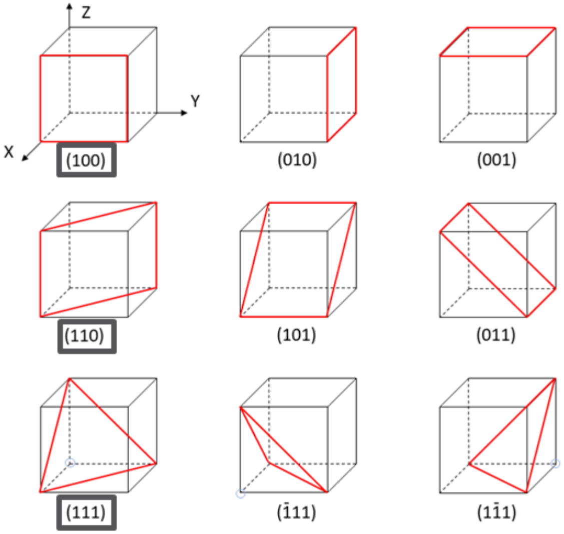
- Prominent cubic facets **{110}**, **{200}**, **{211}**

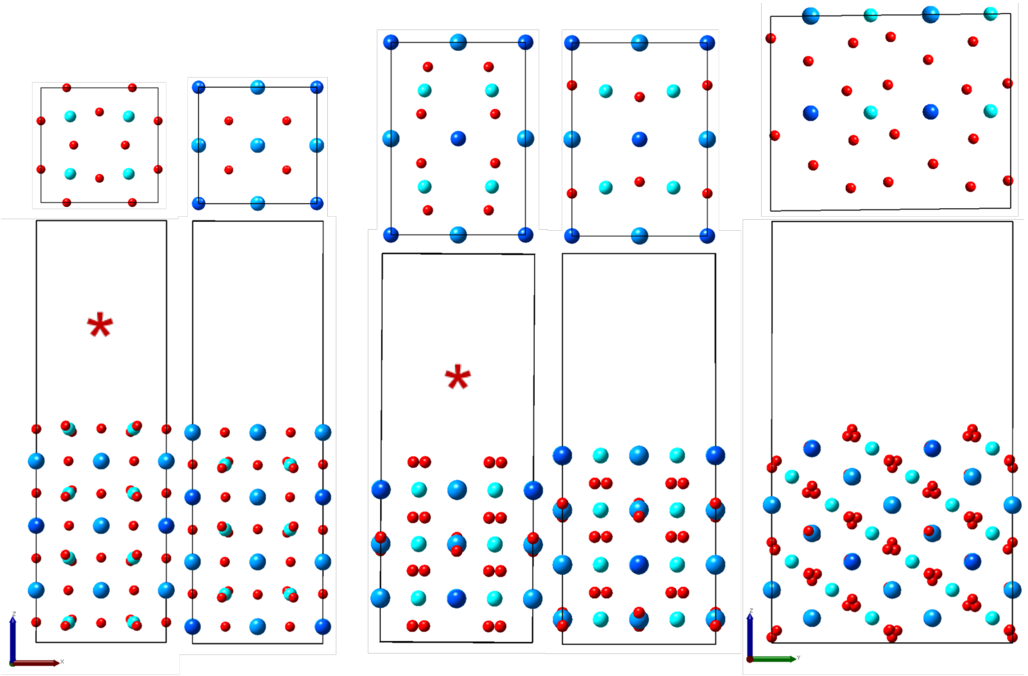
VO_3



$$\sigma = \frac{E_{slab} - n(Ebulk)}{2A}$$

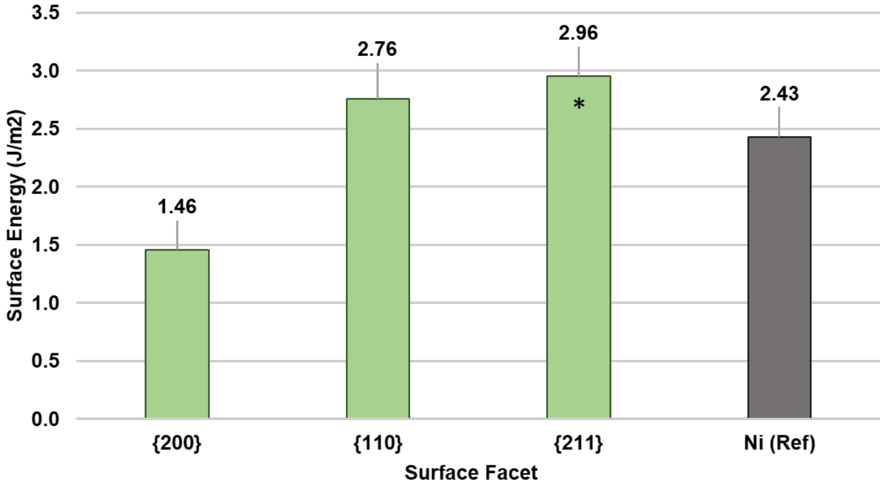
$$\sigma = \frac{E_{slab-V/O} + E_{slab-La/Sr/O}}{2}$$





V/O - {200} La/Sr/O - {200} O - {110} La/Sr/V/O - {110} La/Sr/V/O - {211}

Theoretical Surface Energies of Prominent Oxygen Rich c-LSV



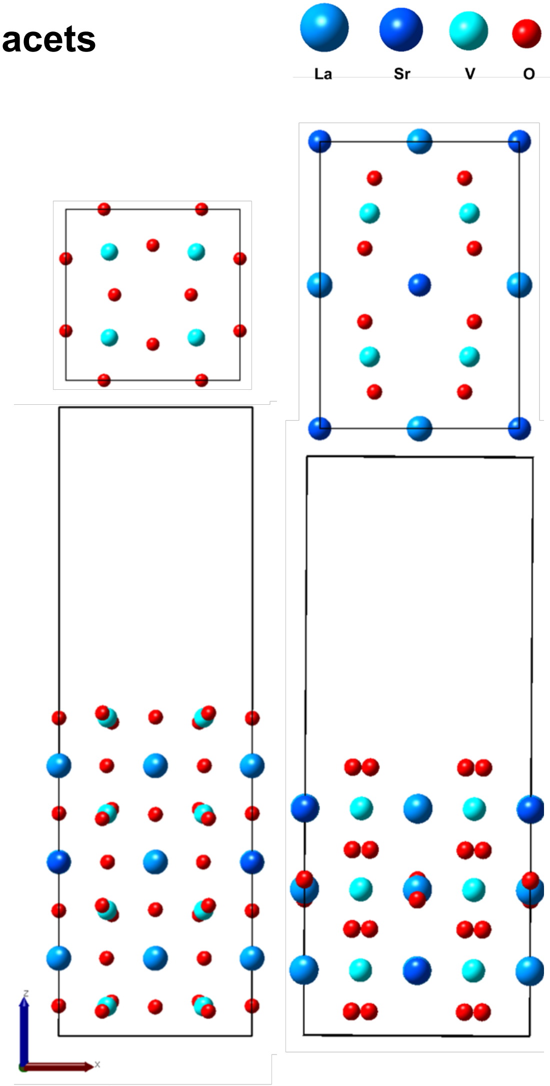
Theoretical Results

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110} Facets

$$E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Ads Site	H2S*	CH4*	CH3OH*
{200} V/O				
	Atop V	-0.45	-0.18	-0.83
	Atop O	-0.43	-0.02	-0.11
	Hollow	0.03	-0.03	-0.09
	Average	**-0.28**	**-0.08**	**-0.34**
{110} La/Sr/V/O				
	Atop La	-1.27	-1.15	-1.80
	Atop Sr	-1.16	-1.12	-1.67
	Bridge O	-0.83	-1.05	-1.63
	Hollow	-1.12	-1.07	-1.66
	Average	**-1.10**	**-1.10**	**-1.69**



V/O - {200}

O - {110}

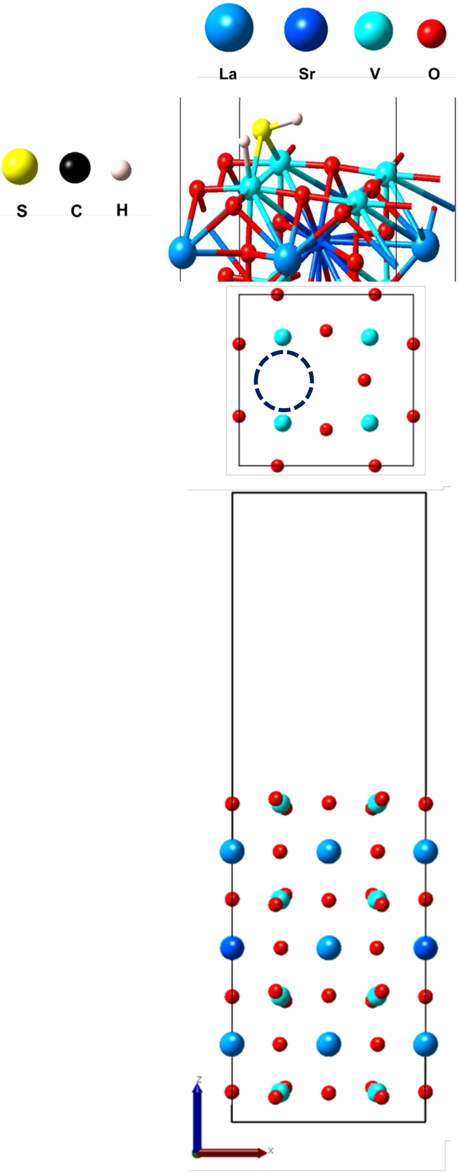
Theoretical Results

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110} Facets

$$E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Ads Site	H2S*	HS*, H*	H*, S*, H*
{200} V/O				
	Atop V	-0.46		
	Atop O	-0.43		
	Atop V_O		-1.70	
	Hollow	0.01		
Termination	**Ads Site**	**CH4***	**H3C*, H***	**CH2*, H*, H***
{200} V/O				
	Atop V	-0.23		
	Atop O	-0.03		
	Atop V_O	-0.46		
	Hollow	-0.04		
Termination	**Ads Site**	**H3COH***	**H3CO*, H***	**H2C*, H*, O***
{200} V/O				
	Atop V	-0.85		
	Atop O*	-0.87		
	Atop V_O	-1.09		
	Hollow	-0.02		



V/O - {200}

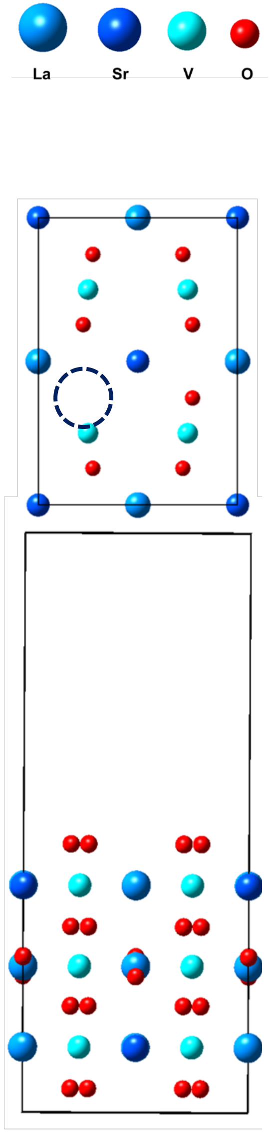
Theoretical Results

Lanthanum Strontium Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Cubic {200}, {110} Facets

$$E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})$$

Adsorption Energy (eV)

Termination	Ads Site	H2S*	HS*, H*	H*, S*, H*
{110} La/Sr/V/O				
	Hollow La	-0.30		
	Hollow Sr	-0.17		
	Bridge O	-0.20		
	Atop V_O	-0.45		
Termination	**Ads Site**	**CH4***	**H3C*, H***	**CH2*, H*, H***
{110} La/Sr/V/O				
	Hollow La	-0.12		
	Hollow Sr	-0.17		
	Bridge O	-0.06		
	Atop V_O	-0.18		
Termination	**Ads Site**	**H3COH***	**H3CO*, H***	**H2C*, H*, O***
{110} La/Sr/V/O				
	Hollow La	-0.69		
	Hollow Sr	-0.90		
	Bridge O	-0.80		
	Atop V_O	-1.15		



O - {110}

Theoretical Results

Lanthanum Vanadate ($La_{0.7}Sr_{0.3}VO_{3\pm\delta}$) – Mixed Cubic {200} H_2S Adsorption

- Higher surface energy with increasing oxygen deficit

$$\boxed{E_f^O = E_{slab\text{-}O} - (E_{slab} + \mu_O)}$$

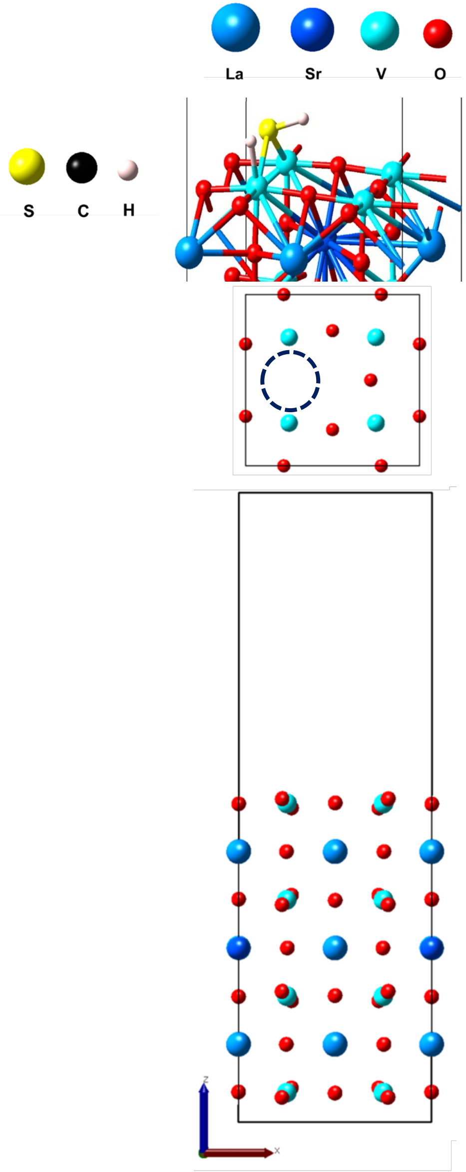
Surface Energy

Termination	Charge	σ (J/m²)	Avg. σ (J/m2)	E_f^O (eV/O atom)
{200} V/O	-7	-0.78	1.46	
	-5	0.62	2.16	5.52
	-3	1.94	2.82	4.95
	-1	3.30	3.50	5.23
	1	4.68	4.19	5.33
{200} Sr/La/O	0	3.70		

$$\boxed{E_{ads} = E_{slab + molecule} - (E_{slab} + E_{molecule})}$$

Adsorption Energy (eV)

Termination	Total Charge	Ads Site	H2S*	HS*, H*	H*, S*, H*
{200} V/O	-7	Atop V_O	-0.43		
	-5	Atop V_O		-1.70	
	-3	Atop V_O		-1.07	
	-1	Atop V_O		-1.06	
	1	Atop V_O		-1.06	



V/O - {200}

Conclusions

Experimental

1. 300-3000ppm C_4H_4S in CH_3OH is 18-113x more sulfur tolerant than Ni-YSZ
   - 300-3000ppm H_2S in CH_4 - 90-164x more tolerant
   - Lower difference between CH_3OH and Ni-YSZ is from methanol
   - Even Ni-YSZ sulfur tolerance is improved, possibly from CH_3OH
   - No significant difference in adsorption until 3000ppm 700C
2. LSV crystal phase does not appear to influence adsorption
3. Additional tests using dimethyl sulfide and diallyl sulfide confirm methanol likely contributing factor to increased sulfur tolerance

Modeling

1. LSV adsorbs H_2S, methane, and methanol through molecular adsorption on oxygen rich surfaces.
2. Slightly stronger adsorption of methanol than H_2S, likely due to higher dielectric constant of methanol.
3. LSV can adsorb H_2S through barrierless one-step dissociative chemisorption, reacting with surface oxygen, leading to La/Sr-SH and V-OH bonds, in presence of oxygen vacancies.
4. LSV adsorbs H_2S on oxygen deficient surfaces through molecular adsorption, as well as with barrierless one-step dissociative chemisorption, reacting with surface La/Sr, leading to La/Sr-SH and La/Sr-OH bond, in the presence of oxygen vacancies.

Acknowledgements

Office of the Chief Scientist, GVSC

Fuel Cell Technologies Branch, GVSC

Fuels and Lubricants Branch, GVSC

Water Treatment and Handling Branch, GVSC

Characterization and Failure Analysis Branch, GVSC

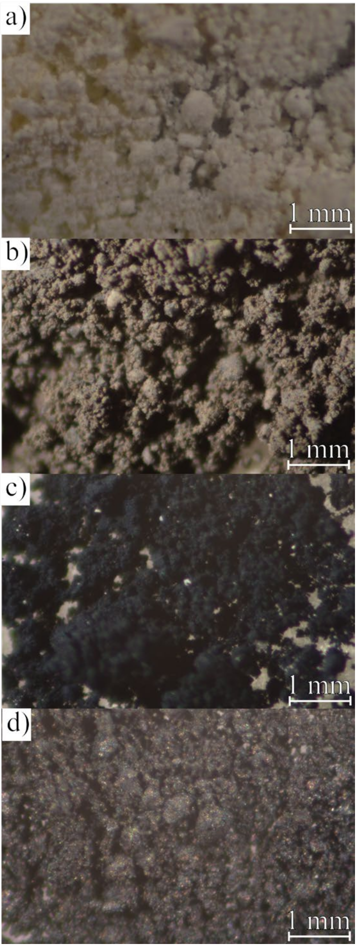
Questions?

Backup Slides

Experimental Results – Adsorption Rates 10vol% 700C

Experimental Results – Optical Microscopy

30ppm



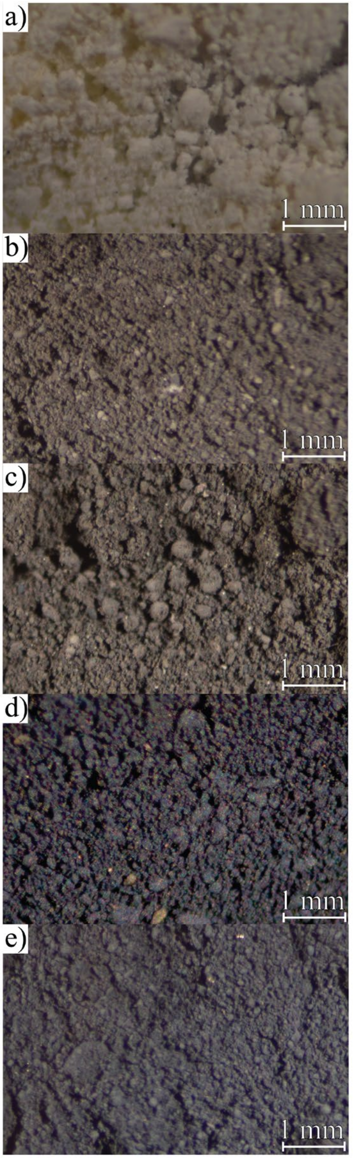
a) Untested LSV Oxide Powder

b) 30ppm H_2S 400°C LSV Oxide

c) 30ppm H_2S 500°C LSV Oxide

d) 30ppm H_2S 700°C LSV Oxide

300ppm



a) Untested LSV Oxide Powder

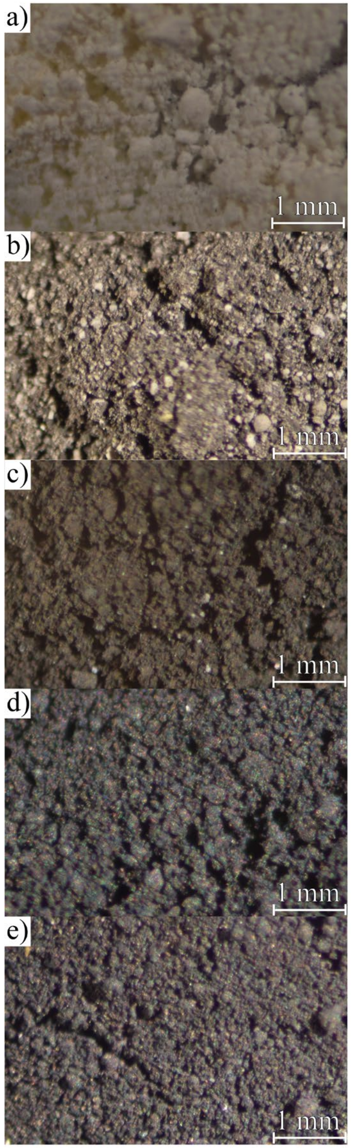
b) 300ppm H_2S 400°C LSV Oxide

c) 300ppm H_2S 500°C LSV Oxide

d) 300ppm H_2S 600°C LSV Oxide

e) 300ppm H_2S 700°C LSV Oxide

10vol%



a) Untested LSV Oxide Powder

b) 10vol% H_2S 400°C LSV Oxide

c) 10vol% H_2S 500°C LSV Oxide

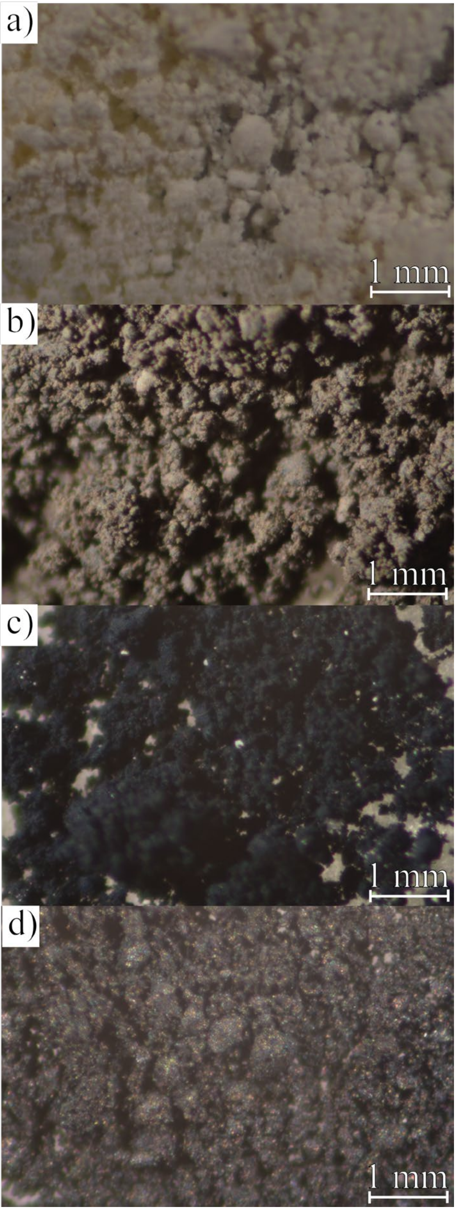
d) 10vol% H_2S 600°C LSV Oxide

e) 10vol% H_2S 700°C LSV Oxide

Experimental Results – Optical Microscopy

La = +3

Sr = +2



Untested
LSV Oxide
Powder

Cream

V = +5

30ppm H_2S
400°C LSV
Oxide

Brown/Yellow

V = +5

30ppm H_2S
500°C LSV
Oxide

Dark Blue

V = +4

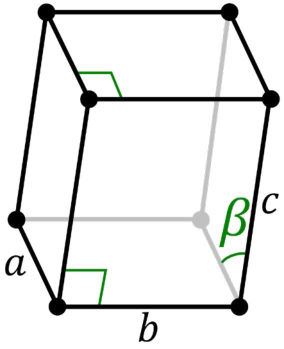
30ppm H_2S
700°C LSV
Oxide

Black

V = +3

Experimental Results – Crystal Structures

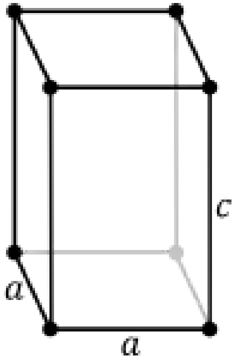
Monoclinic



$a \neq b \neq c$

$\alpha = \gamma = 90 \neq \beta$

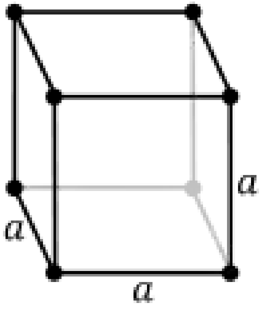
Tetragonal



$a = b \neq c$

$\alpha = \gamma = \beta = 90$

Cubic



$a = b = c$

$\alpha = \gamma = \beta = 90$

Experimental Results – Activation Energy Calculation

$$R_{ads,act} = k * P_{gas,partial}^{x}$$

$$P_{gas,partial} = P_{gas} * X_{H_2S}$$

$$\mathrm{X} = kinetic\ order\ (assume\ 1)$$

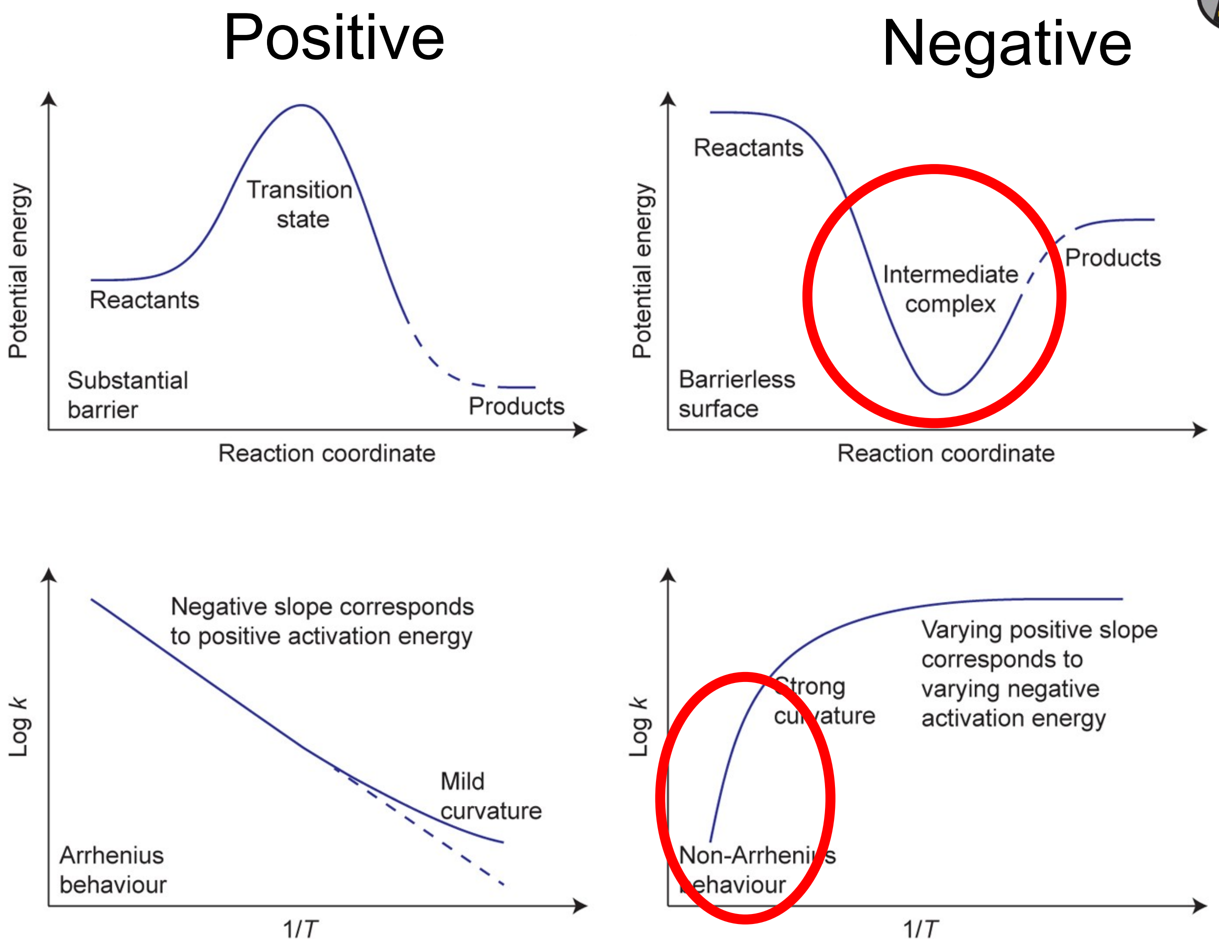
$$\mathrm{k} = kinetic\ rate\ constant$$

$$X_{H_2S} = H_2S\ Mol\ Fraction$$

$$P_{gas} = Gas\ Pressure\ on\ Sample\ (45\ PSI)$$

- Experimental and Kinetic Model Adsorption Rate Assumed Equal
- Kinetic Rate Constant Fitted to Match Experimental Adsorption Rate
  - Rate Constant Used to Determine Activation Energy

Experimental Results – Negative Activation Energy



- Negative Activation Energy
  - Barrierless Reaction
  - Capture of Molecules in a Potential Well
  - Higher Temperature Drives more Molecules from Well
  - Less Negative Value has Greater Reaction Barrier

Experimental Results – Activation Energy Calculation

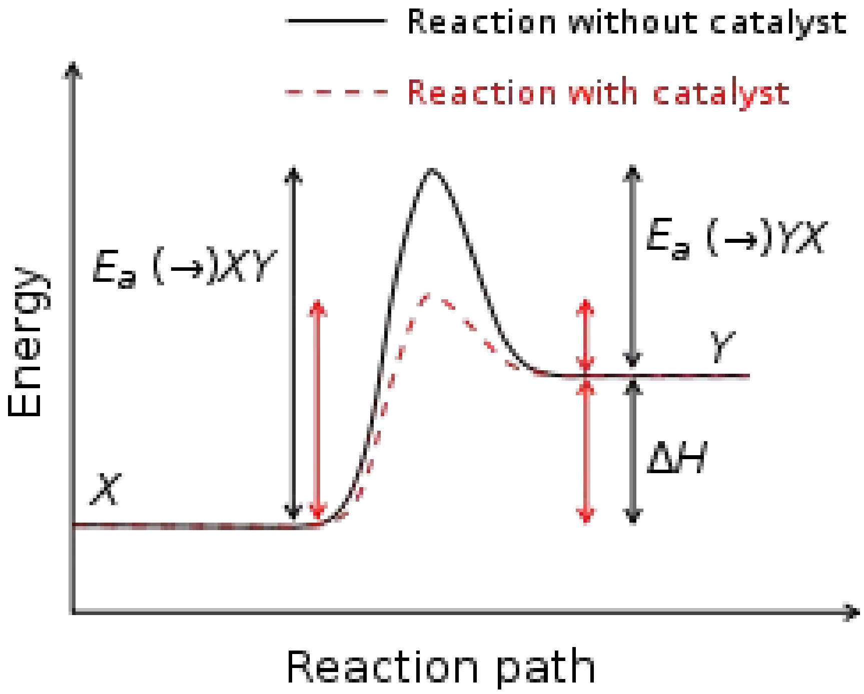
$$k = A * e^{\frac{-E_a}{R*T}} \longrightarrow Ln(k) = \frac{-E_a}{R*T} + Ln(A)$$

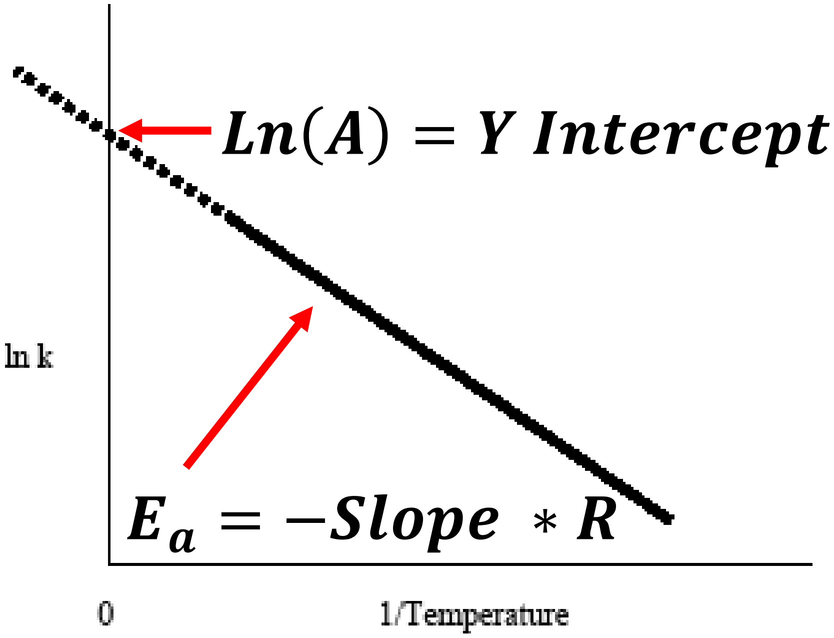
R = Ideal Gas Constant

T = Temperature

E_a = Activation Energy (AE) (Energy Barrier for Reaction to Occur)

A = Pre-Exponential Factor (PEF) (Frequency of Collisions)





$$Ln(A) = Y\ Intercept$$

$$E_a = -Slope * R$$