Development of Modified Nickel-Based Compositions For On-Anode Reforming

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Outline of Presentation

- On-anode reforming—incentives and challenges
- FY05 areas of research
- Review and analysis of recent progress
- Conclusions
- Future work

Incentives for On-Anode Reforming

- Increase efficiency
  - Utilize heat generated from fuel cell energy losses
  - Reduce cell cooling requirements—less excess cathode air
- Reduce system steam requirements
  - Utilize H_2O generated from electrochemical oxidation of H_2
- Use synergy of electrochemical oxidation of H_2 and CO with CH_4 reforming
  - Increase methane conversion by shift of equilibrium
  - Reduce reforming temperature
- Eliminate or reduce size of high temperature external reformer
  - Reduce capital investment and operating costs

Challenges in On-Anode Reforming

- Deactivation through carbon formation
  - Hinders operation at desired low steam-to-carbon (S/C) ratios
- Kinetic mismatch of Ni-YSZ reforming and electrochemical oxidation
  - Reforming rate fast relative to electrochemical oxidation
    - Possible large endotherm at leading edge of cell
    - Potential for warping or cracking cell
- Our work is aimed at finding solutions for above challenges

FY05 Research Accomplishments

- Obtained baseline data on Ni-YSZ for methane and synthetic natural gas steam reforming
  - Activity, activation energy, feed component dependence
  - Activity maintenance—identified sintering effects from H_2O/CH_4 feed
- Evaluated modified Ni-YSZ for reduced carbon susceptibility and low S/C operation
  - Identified MgO modification of Ni-YSZ as stabilizer to Ni sintering and to carbon susceptibility
  - Continuing to assess need for pre-reforming of natural gas feedstock
- Evaluated Cu-modified Ni-YSZ for methane steam reforming activity reduction
  - Achieved activity reduction by more than one order of magnitude compared with Ni-YSZ at 700°C

Catalyst Testing Procedures

- Reactor
  - Tubular quartz, 4mm i.d.
- Catalyst
  - Typical charge 30 mg, 80-100 mesh
  - Dilution with 300 mg YSZ to minimize bed temperature endotherm
  - Pretreatment: typically 700°C for 1 hour in pure H_2
- Feed
  - Typically 3:1 S/C with variable H_2
  - N_2 or He diluent included to allow feed flexibility
    - Maintain constant residence time regardless of feed ratio
  - Natural gas: 96% CH_4, 3% C_2H_6, 1% C_3-C_4
  - Space velocity (GHSV): cc feed/g cat-h

Catalyst Preparation Methods

- Ni-YSZ
  - Standard material: NiO milled with YSZ and calcined at 1375°C
- Ni-MgO and Ni-Cu
  - Standard material: glycine nitrate preparation
    - Nitrate salts admixed followed by GN combustion, 800°C calcination
    - Alternate: milling of separately GN nitrate prepared NiO, MgO
    - For Ni-Cu: generally tested without added YSZ
  - Alternate preparations: impregnation of Ni (GN) by Cu or Mg nitrate
  - Modified materials: vary post-calcination temperature, up to 1375°C

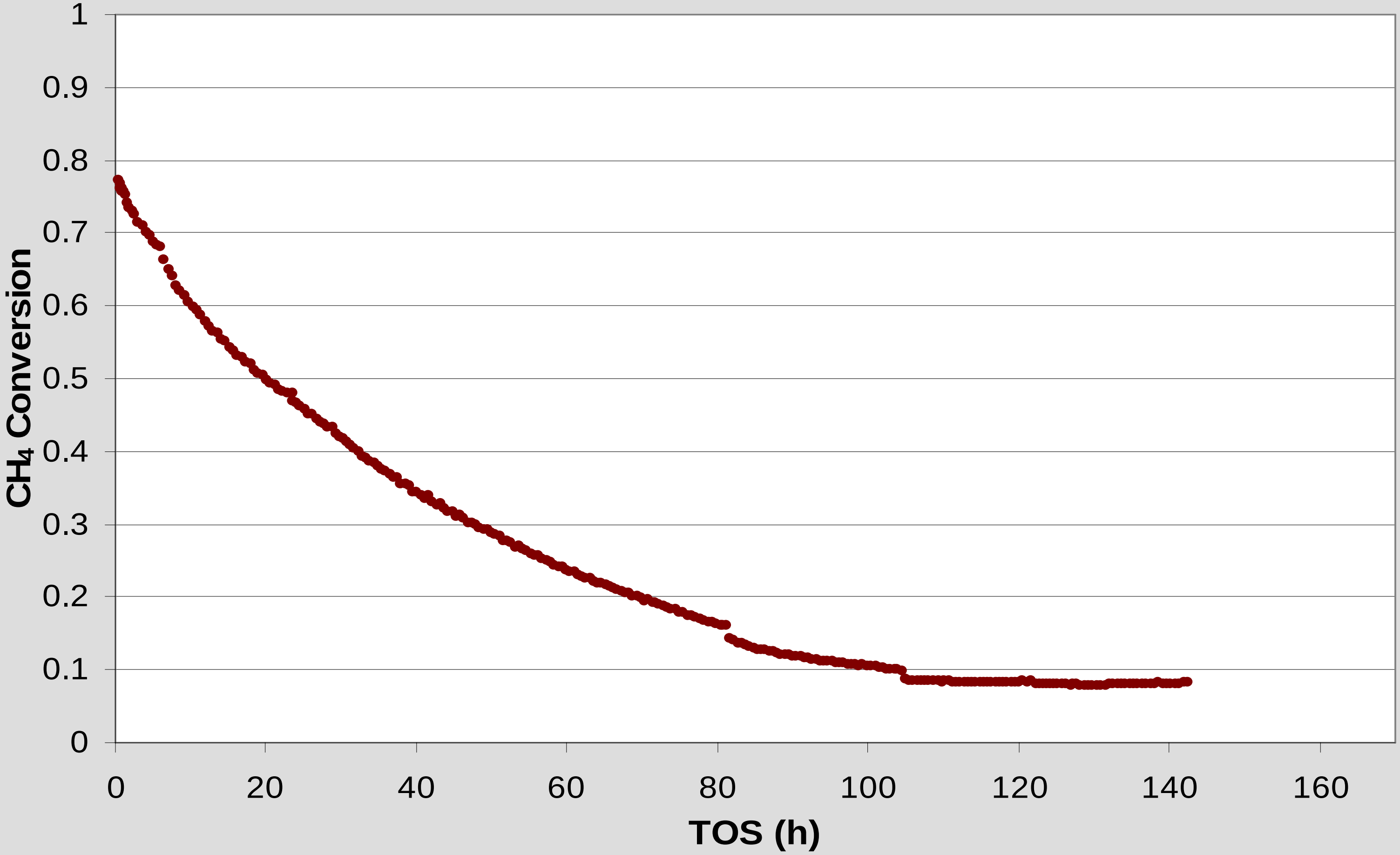
Ni-YSZ Powder Catalyst Testing

Ni-MgO-YSZ Powder Catalyst Testing

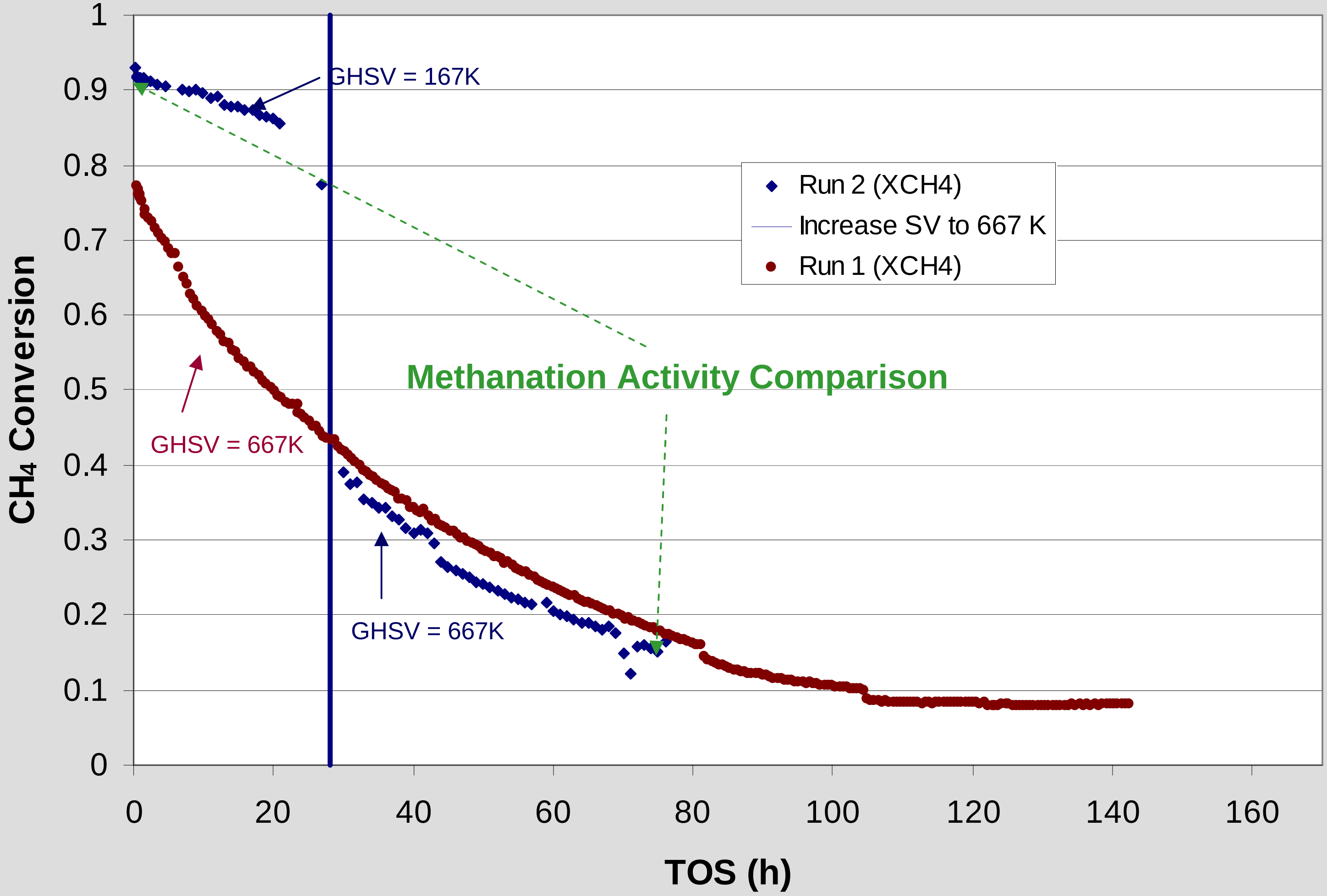
Ni-Cu Powder Catalyst Testing

Ni-YSZ Exhibits Initial Deactivation But Activity Eventually Stabilizes

GHSV = 667K; S/C/H_2/He = 3/1/1/5; T=700ºC

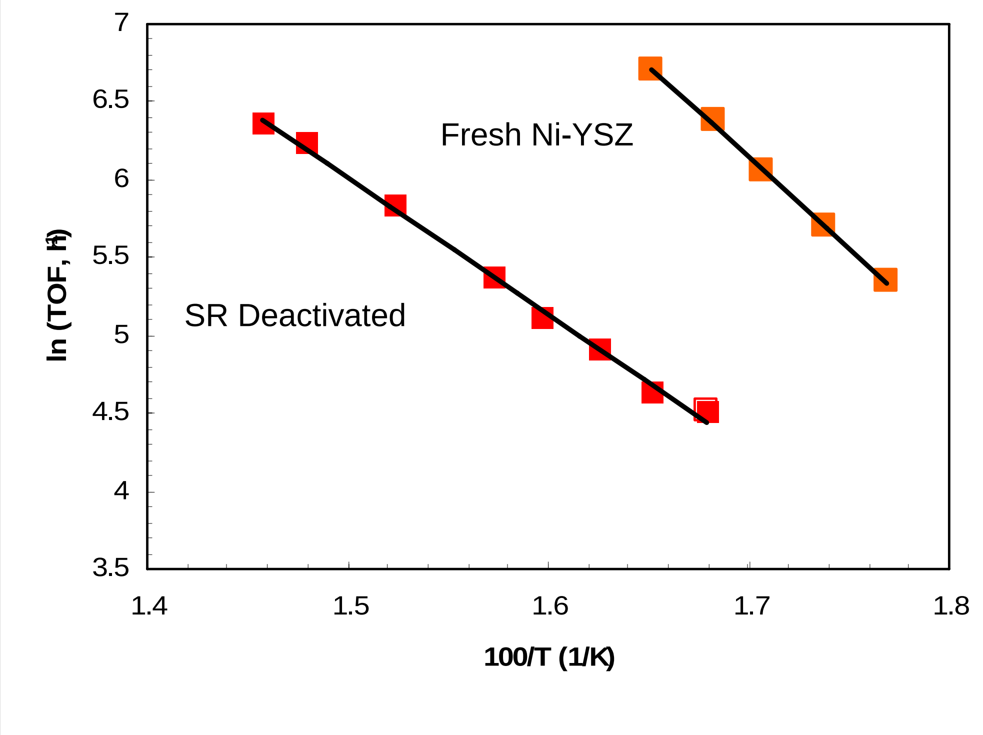


Deactivation of Ni-YSZ is Reproducible



Methanation Activity Comparison

CO Methanation Provides Quantification of Activity Loss



Activation Energy

NiO-YSZ (Baker)	98.06 kJ/mol
NiO-YSZ spent (deactivated)	75.5 kJ/mol

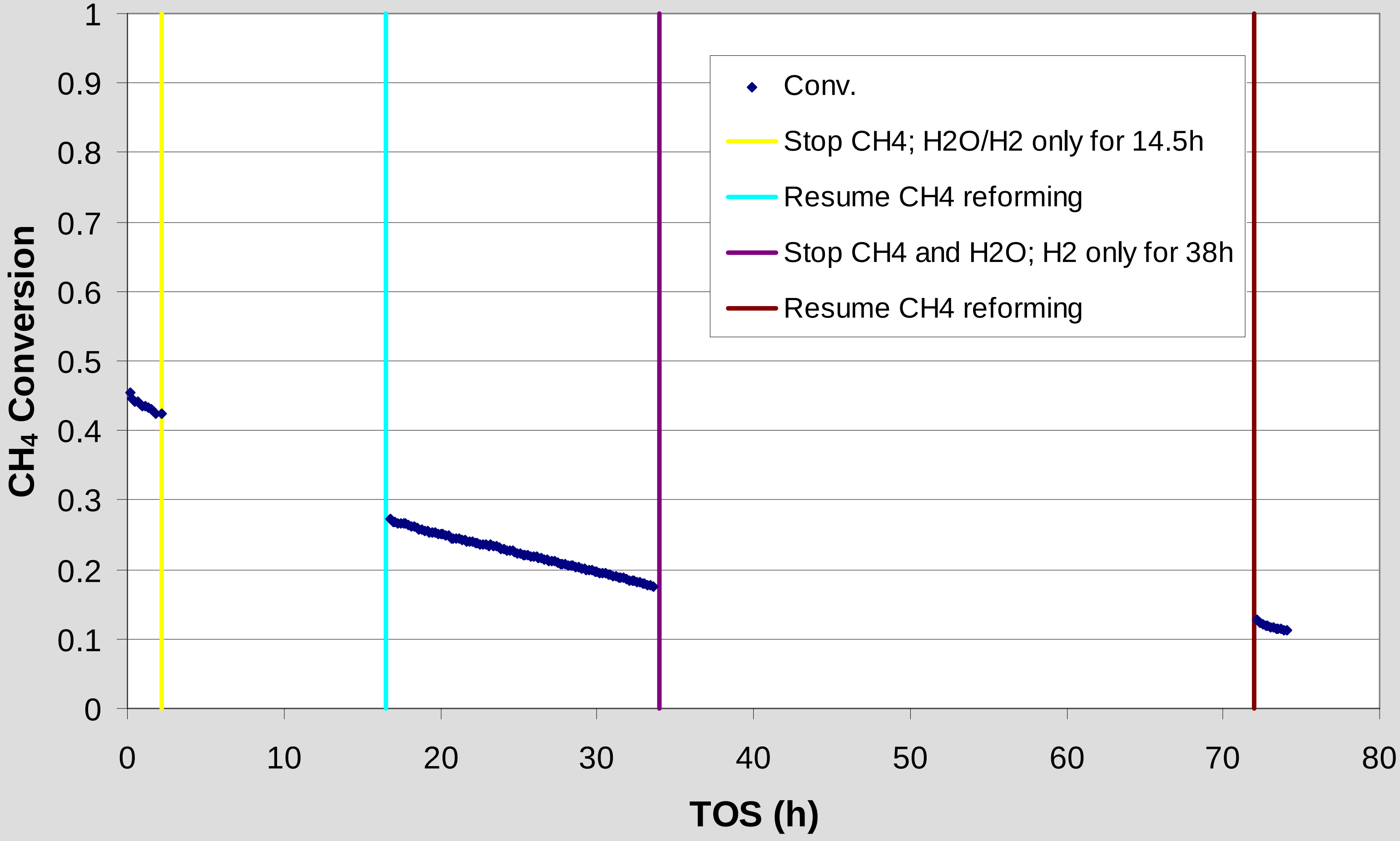
Based on methanation results, assuming all Ni sites has the same turnover number for 30 mg of NiO-YSZ:

~ 12.7 % surface Ni remained after deactivation

Loss of methanation activity parallels steam reforming deactivation

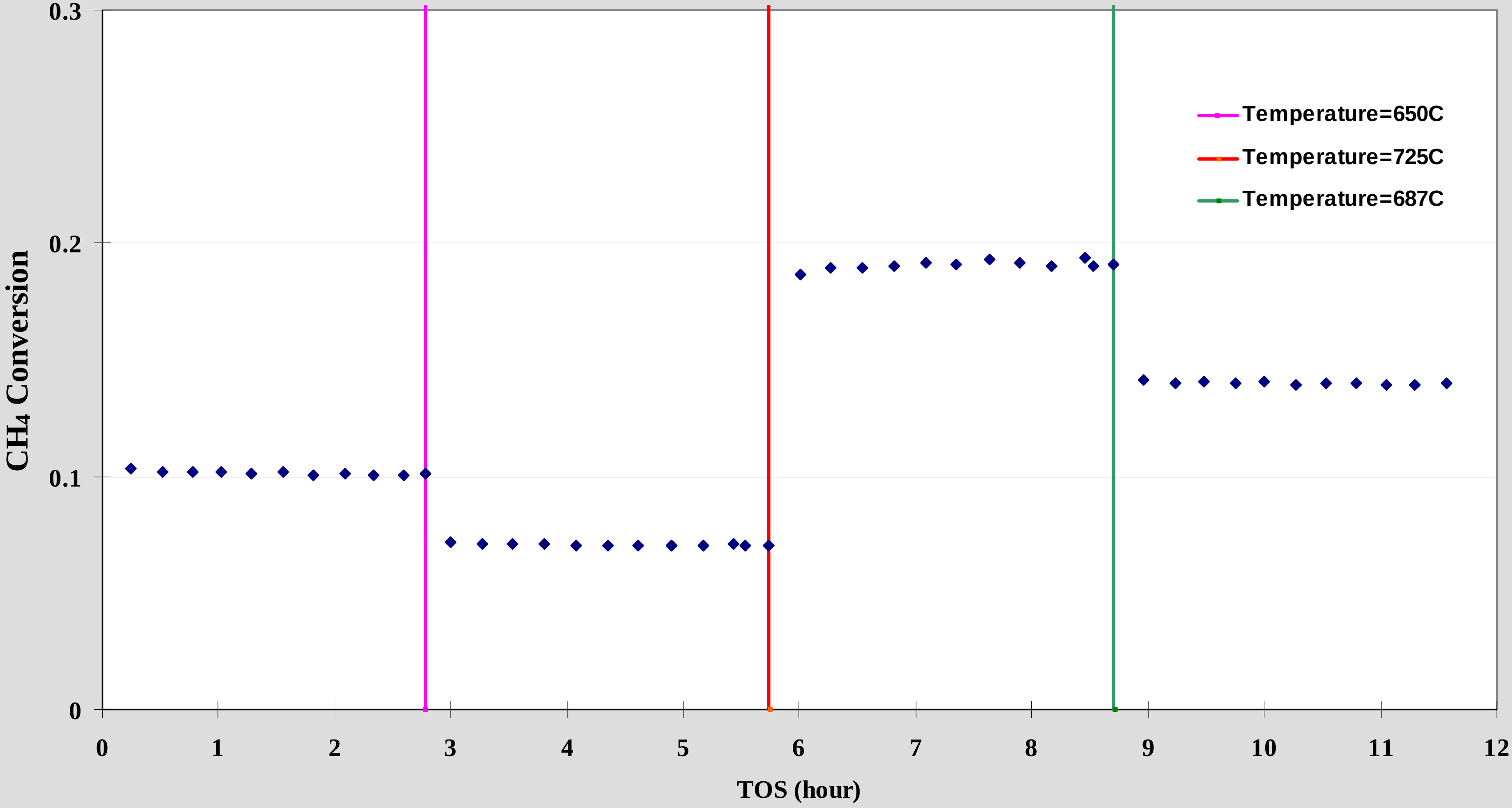
Typical Treatments for Carbon Removal Do Not Regain Activity

SV=667 k ml/g-h, T=700C, $H_2O/CH_4/H_2/He=3/1/1/5$



Lined-out Ni-YSZ Shows Temperature Dependence Typical of Ni Catalysts

Initial Conditions: T = 675°C, GHSV=334K ml/(h*g), S/C/H=3:1:1



E_a = 26.93 kcal/mol

Pretreatment History Impacts on Ni-YSZ Lined Out Activity

Catalyst Pretreatment	Gas composition S/C/H	GHSV (space velocity)	Lined-out conversion, %
700C in H_2, 1h	3/1/6	326K	15
700C in H_2, 1h	3/1/6	328K	12.5
700C in H_2, 1h	3/1/3	328K	14.0
700C in H_2, 1h	3/1/1	334K	12.7
700C in H_2,/H_2O, 7h; 700C in H_2, 1h	3/1/6	334K	<11

S/H_2 ratio has little impact on lined out conversion

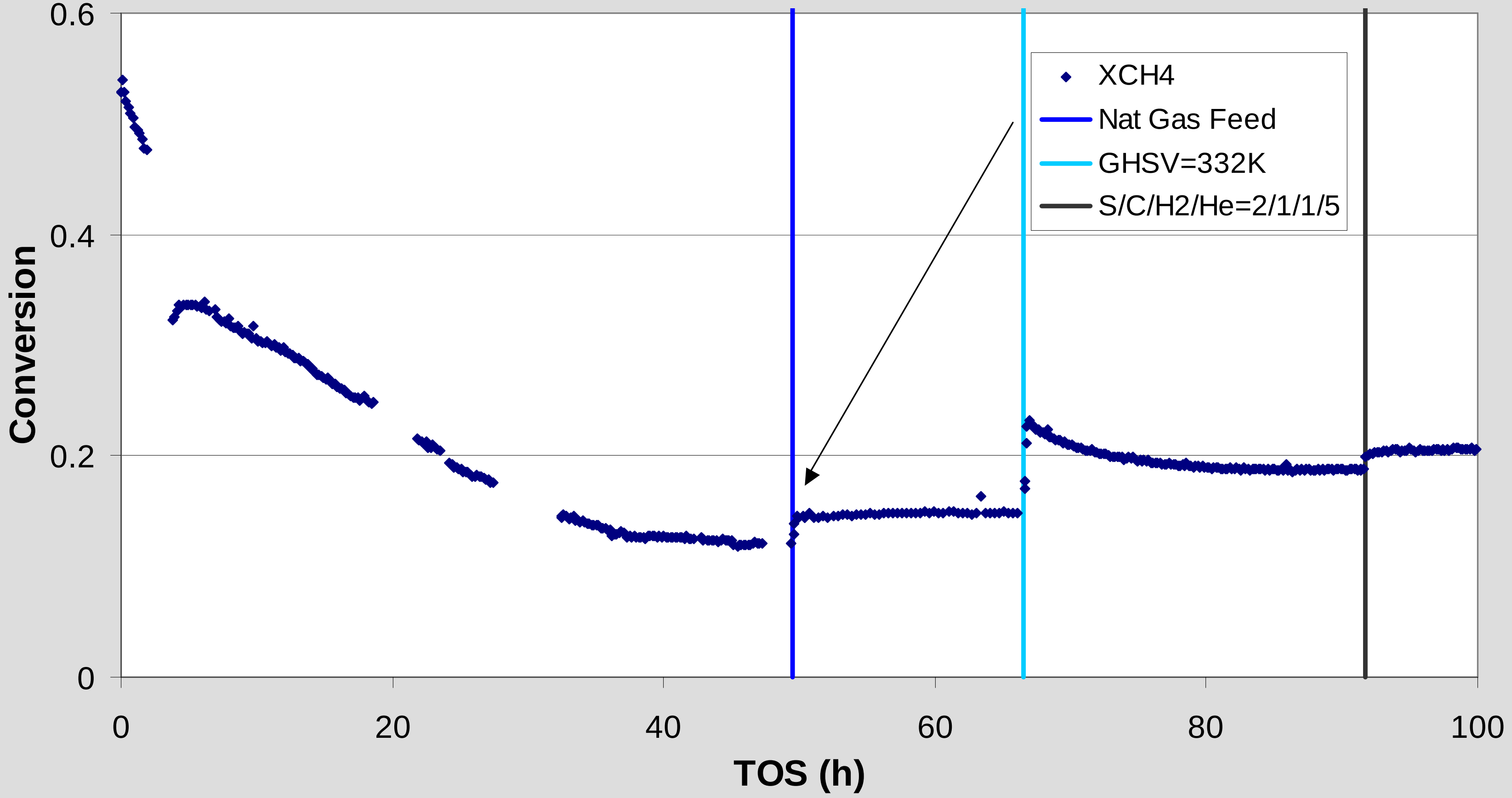
H_2O/H_2 treatment has greater effect

Average turnover rate = 0.194 moles CH_4/g cat-h at 700°C

(exceeds literature value 0.02 moles CH_4/g cat-h at 700°C (Lee et. al., I&EC Research 1990, 29(5), 766-773))

Equilibrated Ni-YSZ Shows Stability Toward Synthetic Natural Gas

Initial GHSV = 667K, S/C/H_2/He = 3/1/1/6, 700°C



No carbon observed in catalyst bed at end of run

Ni-YSZ Methane Steam Reforming Powder Tests--Conclusions

- Initial activity decline, possibly due to sintering or restructuring facilitated by H_2O/H_2*
- Catalyst achieves stable activity (equilibrates) after several to 10’s of hours
- Kinetic parameters for lined-out Ni-YSZ consistent with results from supported Ni catalysts
    - Activation energy ~27 kcal/mol
    - First order in CH_4; zero order in H_2O for S/C>1

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* Consistent with studies of supported Ni catalysts. See J. Sehested, “Sintering of nickel steam-reforming catalysts”, J. Catalysis 2003, *217*, 417-426.

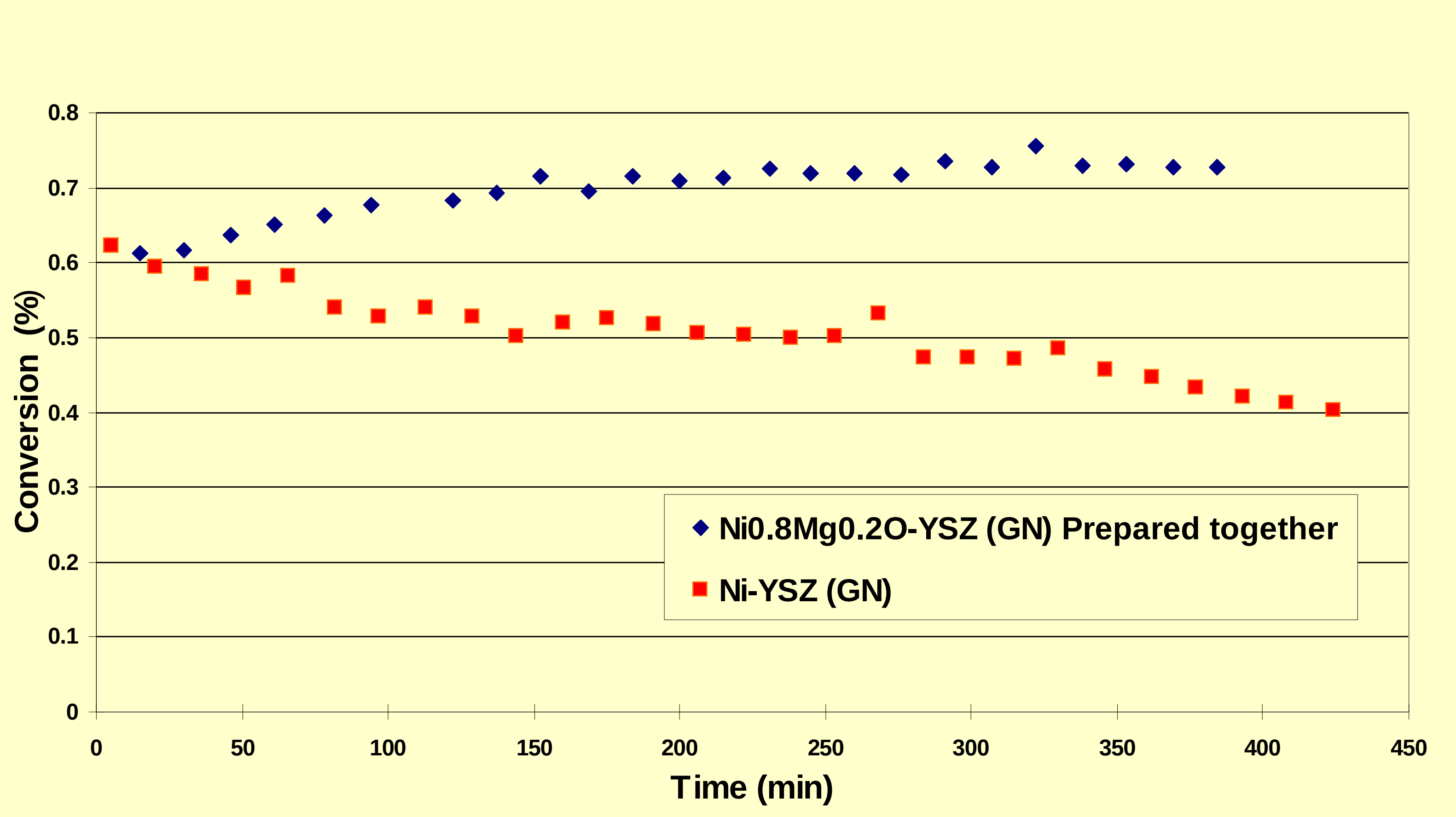
Ni-YSZ Powder Catalyst Testing

Ni-MgO-YSZ Powder Catalyst Testing

Ni-Cu Powder Catalyst Testing

Effect of Addition of MgO on Stability of Ni-YSZ Anode Catalyst (GN Method)

800ºC Calcination, 700ºC, 646K ml/h-g, S/C/H = 3/1/0.1



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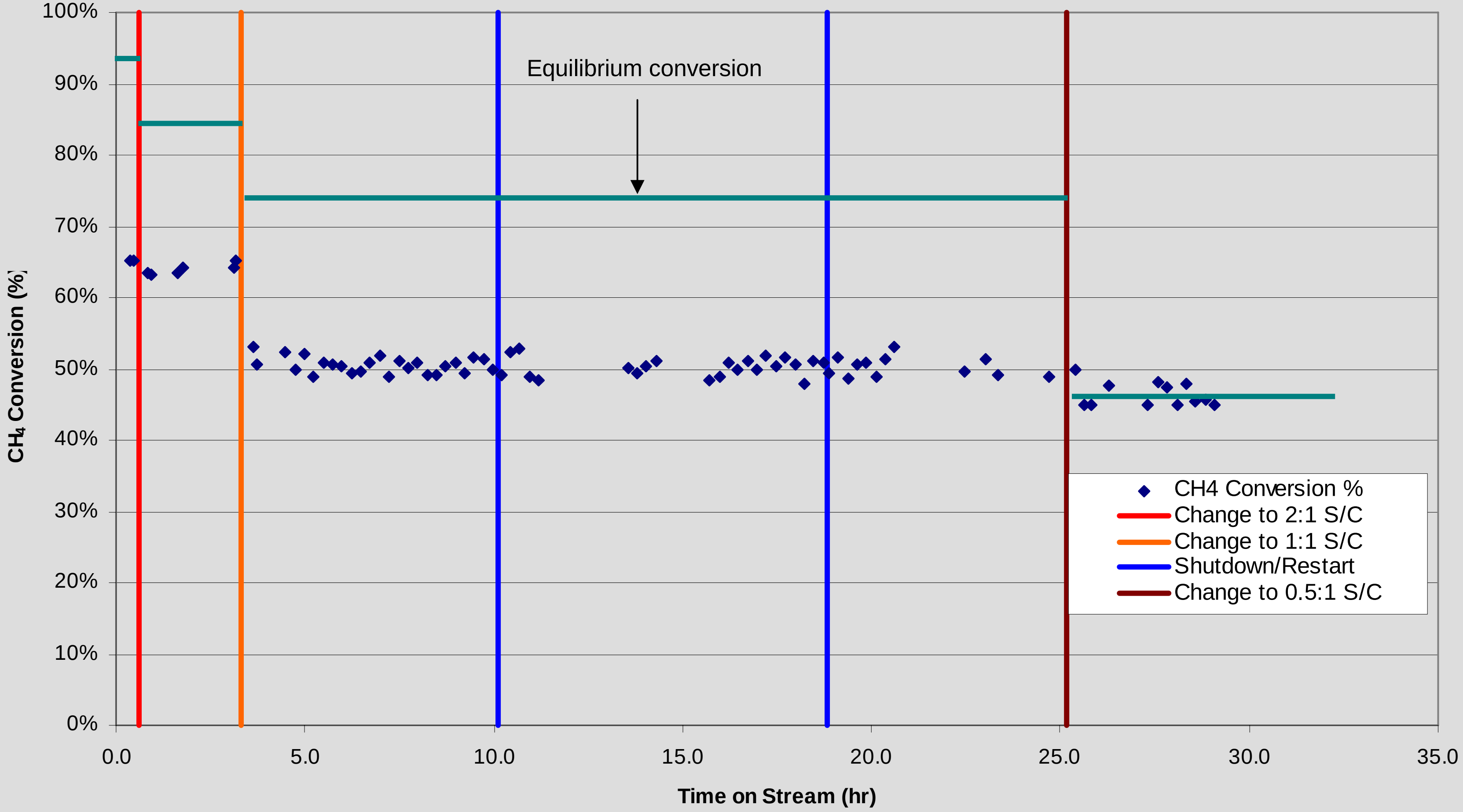
CH_4 Conversion Over 0.8Ni 0.2MgO-YSZ Shows Stability at S/C = 1

WHSV = 701K, S/C/H (Initial) = 3/1/0.1, 670ºC,



Method of Addition of MgO to Ni-YSZ Affects Catalyst Activity and Stability

Catalyst Composition	Pretreatment	GHSV	Conversion, %	Comments
Ni-YSZ	1375C calcine; 700C in H_2, 1h	621K	12-15	Decrease to line out
NiO 0.8-MgO 0.2 GN-YSZ	800C calcine; 700C in H_2, 1h	646K	72	Increase to line out, stabilized high activity
NiO 0.8-MgO 0.2 GN-YSZ; Ni and Mg GN separately, mechanically mixed	800C calcine; 700C in H_2, 1h	626K	≤41	Decrease to line out, but not fully lined out at 13h
Ni-YSZ impregnated Mg nitrate	800C calcine; 700C in H_2, 1h	636K	<15	Decrease to line out, similar to Ni-YSZ
NiO 0.8-MgO 0.2 GN-YSZ	1100C calcine; 700C in H_2, 1h	164K	9	Conversion increases to 45% at 655K at 800C

Ni-MgO-YSZ Methane Steam Reforming Powder Tests--Conclusions

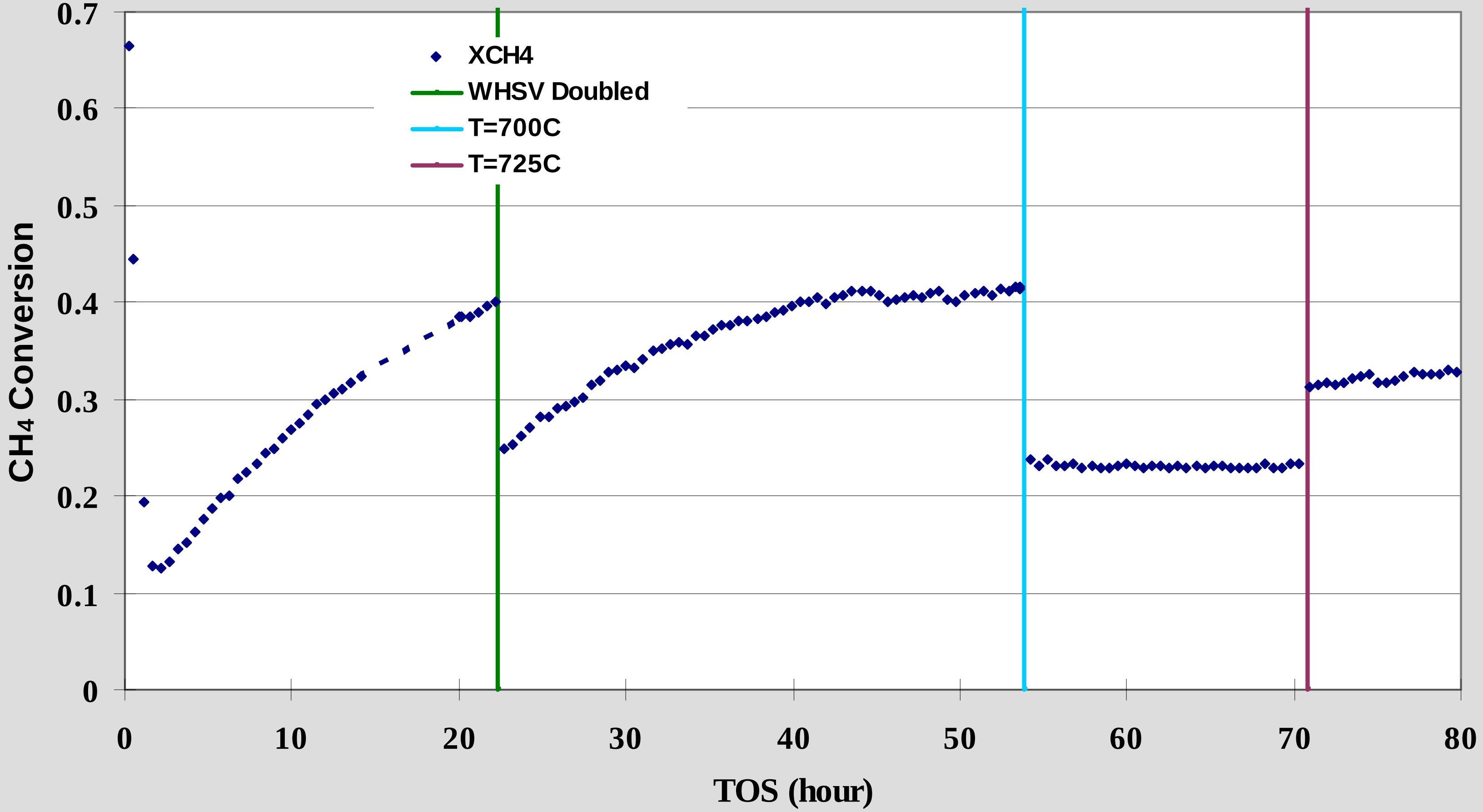
- MgO shows promise as additive for activity stabilization and carbon control
  - Finely dispersed MgO (20%) in Ni shows stable (high initial) activity
    - Well-dispersed MgO retards Ni sintering/restructuring in H_2O/H_2
    - Stable CH_4 reforming obtained at S/C = 1 for ~20 hours
- Method of MgO introduction is important for catalytic performance
  - Activity and stability observed in the following order:

    NiO-MgO(GN)-YSZ > NiO (GN) + MgO (GN)-YSZ > Ni-YSZ + MgO (impreg)
- Calcination temperature affects performance of Ni-MgO-YSZ
  - "$NiMgO_2$" solid solution forms at or below 1100ºC
  - Activity slowly increases with time as Ni becomes reduced and available

Ni-YSZ Powder Catalyst Testing
Ni-MgO-YSZ Powder Catalyst Testing
Ni-Cu Powder Catalyst Testing

98%Ni-2%Cu (GN) After 1375ºC Calcination Shows Loss of Cu Efficacy

T_{init} = 750ºC; S/C/H = 3/1/1; $WHSV_{init}$ = 81,700

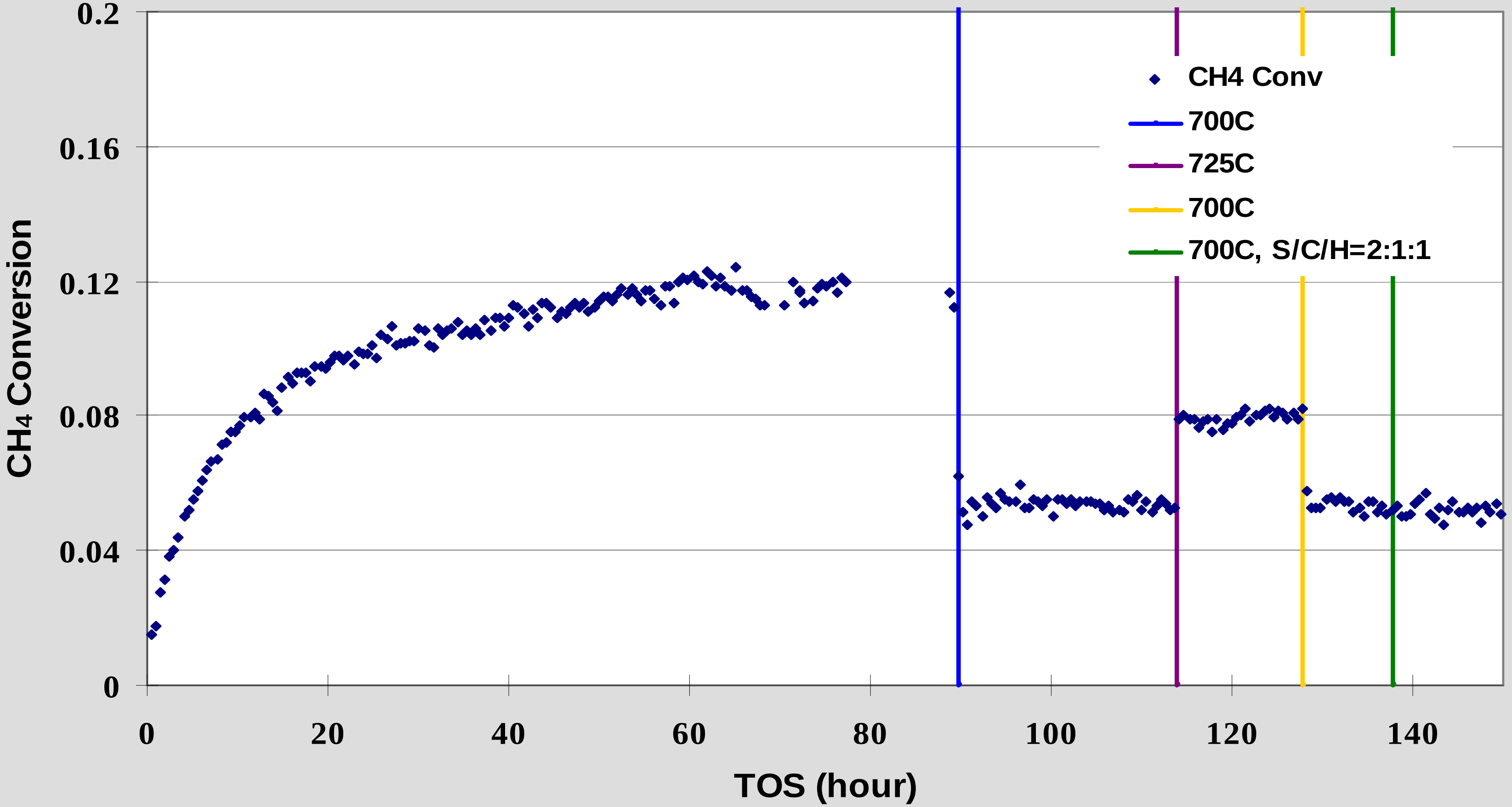


Ea = 32 kcal/mol; compare with 12% conversion at 667K GHSV for Ni-YSZ

Loss of CuO by evaporation at 1375ºC implicated

Catalyst with An Initial Composition of 80%Ni-20%Cu (GN) Calcined at 1375ºC Maintains Reduced Activity

GHSV = 82,000; T_{init} = 750ºC; $S/C/H_{init}$ = 3/1/1



Ea = 36.3 kcal/mol; compare 700ºC result with 12% conversion at 667K GHSV for Ni-YSZ
Some Cu retained following 1375ºC calcination

Cu Addition Method and Pretreatment Affect Ni Activity

Cu Content and Prep Method	Calcination-Reduction	Temp, C	Space Velocity, K	CH_4 Conversion, %	Normalized Rate
2% Cu; GN	800C 4h-700C 1h	700	312	1.5	0.093
2% Cu; GN	800C 4h-900C 3h	700	83	12.5	0.21
2% Cu; GN	1375C 1h-700C 1h	700	163	23	0.81
20% Cu; GN	800C 4h-700C 1h	750	81	1.9	0.012
20% Cu; GN	1375C 1h-700C 1h	700	82	5.5	0.079
20% Cu impregnated on Ni-YSZ	800C 4h-700C 1h	700	166	20	0.69
Ni-YSZ	1375C 1h-700C 1h	700	328	15	1

Ni-Cu Methane Steam Reforming Powder Tests--Conclusions

- Cu shows promise for decreasing activity of Ni-YSZ
  - Glycine nitrate synthesis
  - Activity decrease at 700°C nearly two order of magnitude with 20% Cu
- Effectiveness of Cu decreases with increasing temperature
  - Phase segregation and/or high mobility of Cu at higher temperatures implicated
  - Activation energy of Ni-Cu is higher than Ni-YSZ
- Developing realistic preparation method key to viable Ni-Cu-YSZ anode
  - Volatility of CuO at sintering temperatures requires post-addition of Cu or alternative method of synthesis
  - Simple Cu impregnation method inadequate

Future Work
Carbon Tolerance Studies

- Extended runs to determine Ni-YSZ susceptibility to carbon formation
  - S/C and conversion level effects for methane and natural gas reforming
  - Provide baseline data for comparison with alternate formulations

- Evaluate Ni-MgO-YSZ formulations for improved carbon tolerance
  - Determine effect of preparation and pretreatment on
    - Activity and lineout behavior
    - Carbon-free operation
  - Compare with Ni-YSZ baseline data

- Corroborate/correlate powder results with Ni-YSZ and Ni-MgO-YSZ anode strips

Future Work
Activity Modification Studies

- Determine limits to Ni-YSZ activity control through thermal steam/hydrogen pretreatment

- Extend studies of Ni-Cu-YSZ activity control
  - Cu concentration and pre-treatment effects
  - Temperature cycling studies 700-850°C for activity and stability
  - Stability to low S/C and natural gas
  - Effect of YSZ on Ni-Cu interaction

Future Work
Ni-Cu-YSZ Synthesis and Fabrication

- Evaluate preparation methods for Ni-YSZ-Cu
  - Infiltration or electrodeposition of Cu onto Ni-YSZ post-sintering
  - Other approaches including industry collaboration
- Tailored compositions that compensate for Cu loss during sintering
- Test compositions as powders and formed strips
  - Compare with GN results
  - Measure thermal axial profile and compare with model predictions
- Work with industry to evaluate Ni-Cu-YSZ in cell tests

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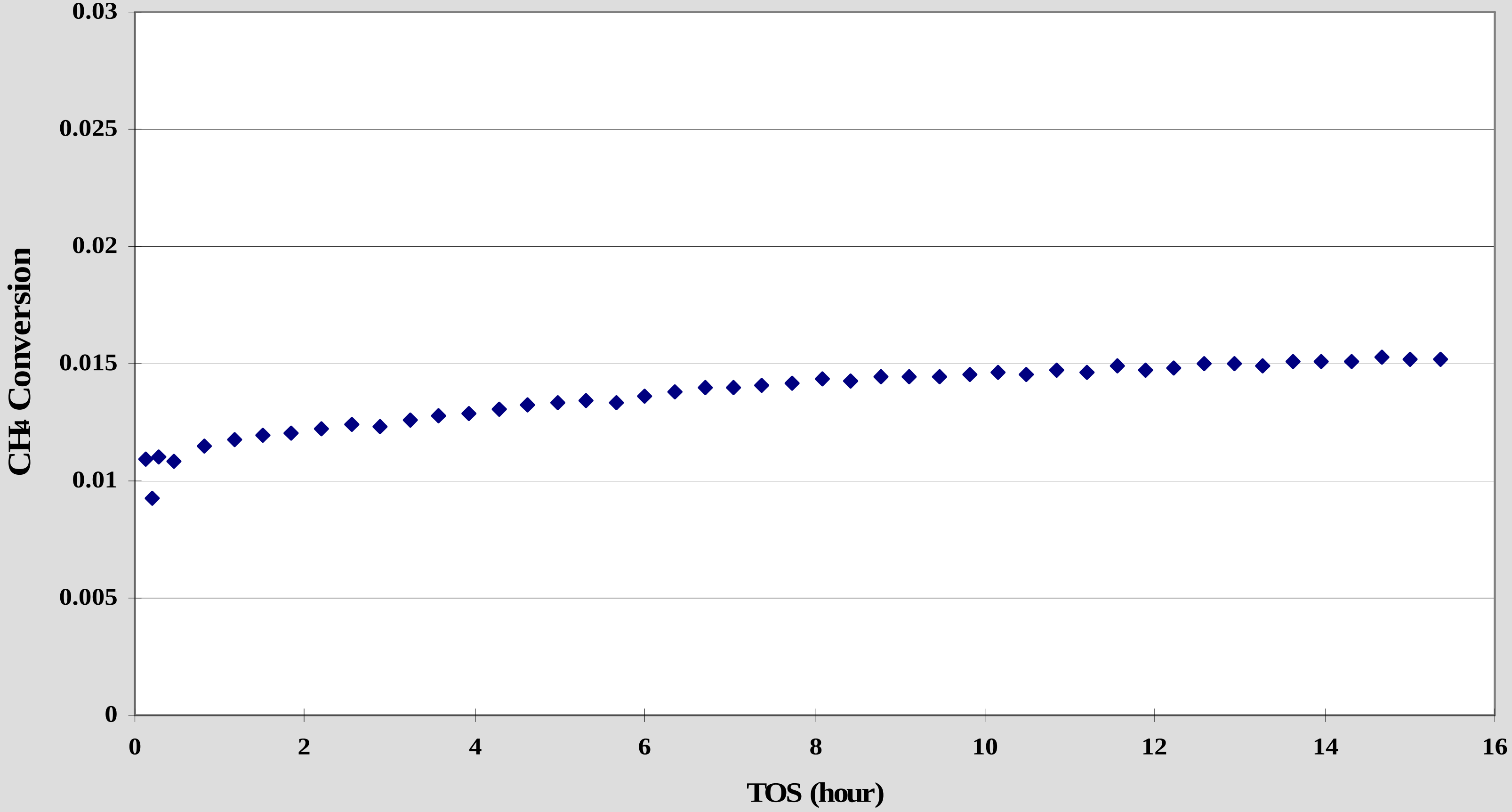
- Additional PNNL contributor: V. Sprenkle provided anode compositions used in our tests.

Backup Slides

Ni0.98Cu0.02 Catalyst Shows Low Activity

GN, Calcined at 800C/4hr,

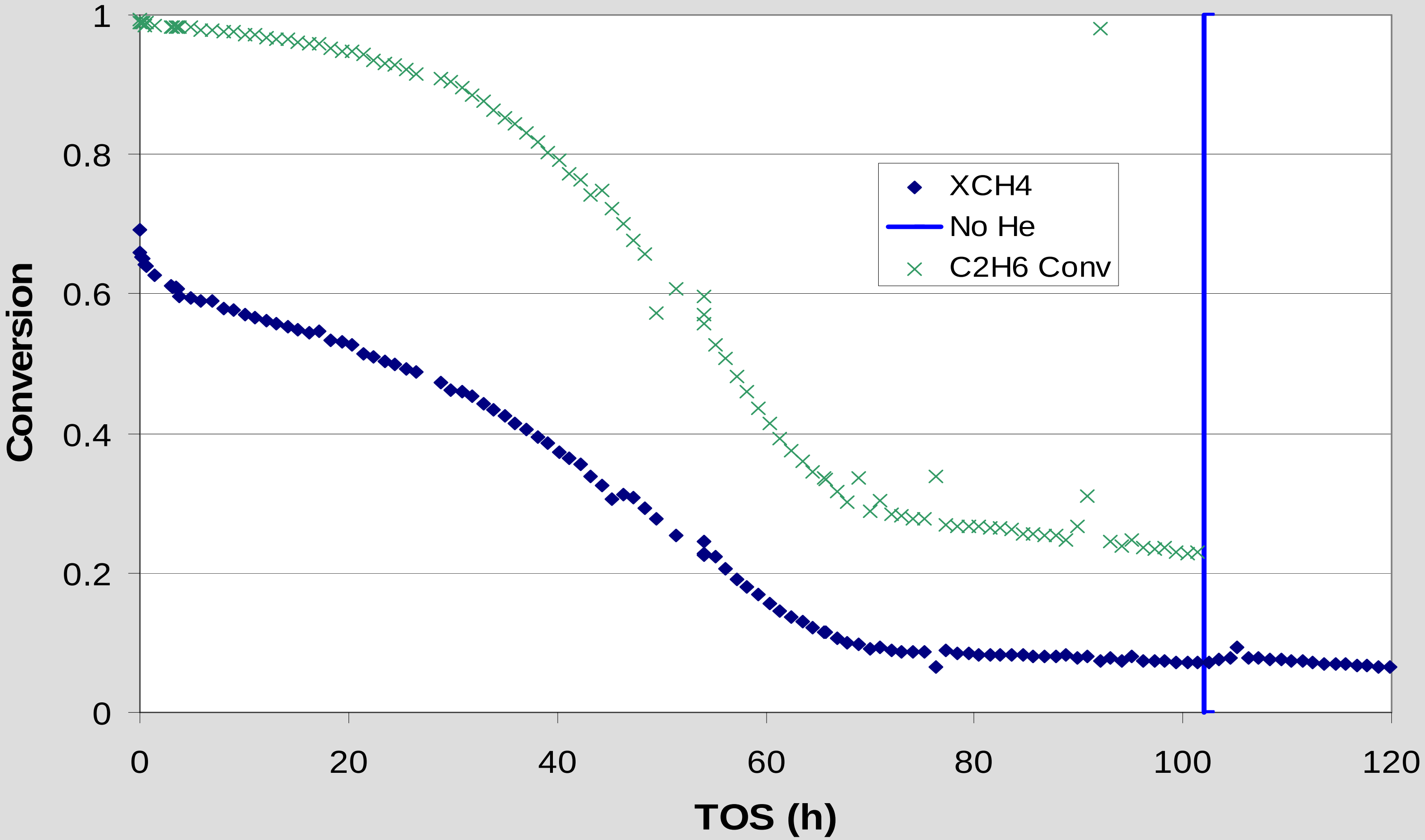
WHSV = 312,400 S/C/H=3:1:0.1 T=700ºC



Compare with 12-15% CH_4 conversion for Ni-YSZ

Conversion of Synthetic Natural Gas over Non-Equilibrated Ni-YSZ Shows Slow Deactivation

GHSV = 667K, S/C/H/He = 3/1/1/5, T=700ºC



Carbon observed at front end of catalyst bed at end of run