

Thermally Stable Ultra-Low Temperature Oxidation Catalysts

János Szanyi, Chinmay Deshmane, Diana Tran, Charles H.F. Peden, Chang Kim, Se Oh, Steve Schmieg, Wei Li

Pacific Northwest National Laboratory

General Motors Research

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**Project ID #
ACE078**

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Overview

► Timeline

- Start – Oct 2013
- Finish – Sept 2016
- 36-month CRADA

► Budget

- Total project funding
 - DOE: \$750k (\$250k/year)
 - GM (\$450k)

► Barriers

- Develop ultra low-temperature oxidation catalysts
- Better understand active site and structure requirements in oxidation catalysts
- Understand deactivation mechanisms
- Design and model catalyst functions and structures

► Partner

- General Motors

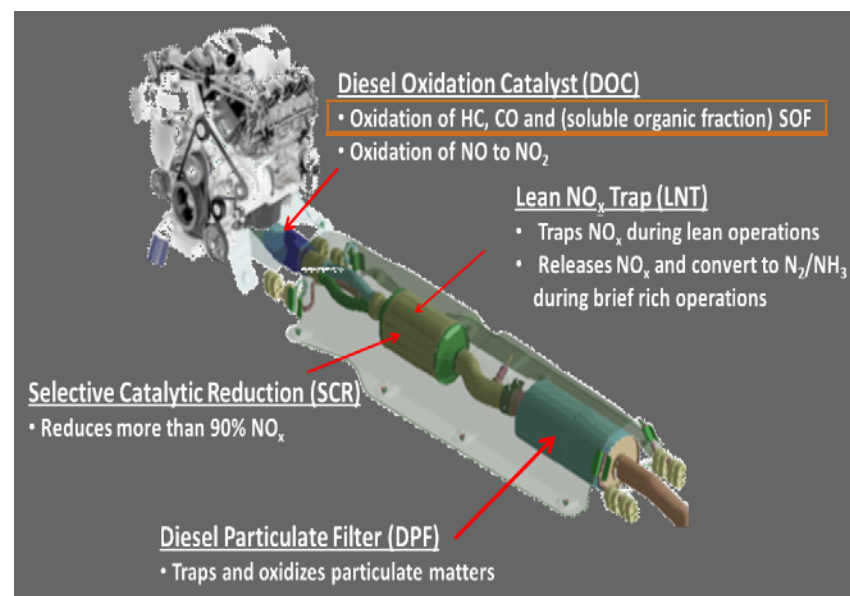
Motivation and Relevance

- ▶ High efficiency engines often implies lower exhaust temperature (T), requiring better low-T catalysis to meet emission regulations by inexpensive and reliable CO/HC/NO_x emission control:

- Removal of CO and unburned HC is required at low exhaust T (< 150 °C).
- High T stability and poison resistance are required as well.

- ▶ PGMs are the most active CO/HC oxidation catalysts at high T, but poisoned by strong CO adsorption at low T.

- PGM commodity pricing is high and volatile. Thrifting or replacement of PGM in oxidation catalysts is desired for:
 - Low T CO/HC oxidation activity
 - cost reduction as an enabler to advanced after treatment and combustion technologies
 - alternative technologies for oxidation reactions



Objectives

This CRADA project aim was to ***develop ultra low temperature CO/HC oxidation catalysts with sufficient high temperature hydrothermal stability.***

- ▶ Improve the understanding of the nature and structure of active sites in CuO/metal oxide catalysts intended for CO/HC oxidation
- ▶ Understand
 - the effects of synthetic methods on composition and structure of catalysts and on their effectiveness in CO/HC oxidation.
 - the mechanisms of activity decline under practical operating conditions and regeneration
 - sulfur poisoning mechanism
- ▶ Test alternative catalyst formulations (CoO_x ; MnO_x)

Accomplishments

- ▶ Completed **catalytic reaction** tests (CO and HC oxidation) on both GM-prepared and PNNL-made catalysts
 - Catalyst formulation, aging and sulfur poisoning by GM
- ▶ Alternative **synthesis** methods
 - Characterize composition, structure, reactivity and active sites
- ▶ Performed detailed **characterization** on selected catalysts
 - **XPS**: Composition and redox properties
 - **FTIR**: characterization of active sites by probe molecule adsorption/reaction.
 - **XRD**: phase identification and variation during thermal aging, sulfur poisoning
 - **TEM/EDX**: morphology and active phase dispersion
- ▶ Completed **DFT** studies on oxygen vacancy formation, sulfure poisoning and possible reaction mechanisms

Collaboration: with GM - CRADA

- ▶ Based on research reported by GM
 - CRADA initiated for PNNL assistance leveraging surface science, preparation and catalyst characterization capabilities
 - Analytical assessment and computational model
- ▶ Scope split, but coordinated between GM and PNNL
 - **GM** - Catalyst
 - formulation:** metal oxides (CuO on ceria/zirconia-based supports)*
 - aging:** hydrothermal; deactivation; poisoning*
 - testing:** CO and HC oxidation*

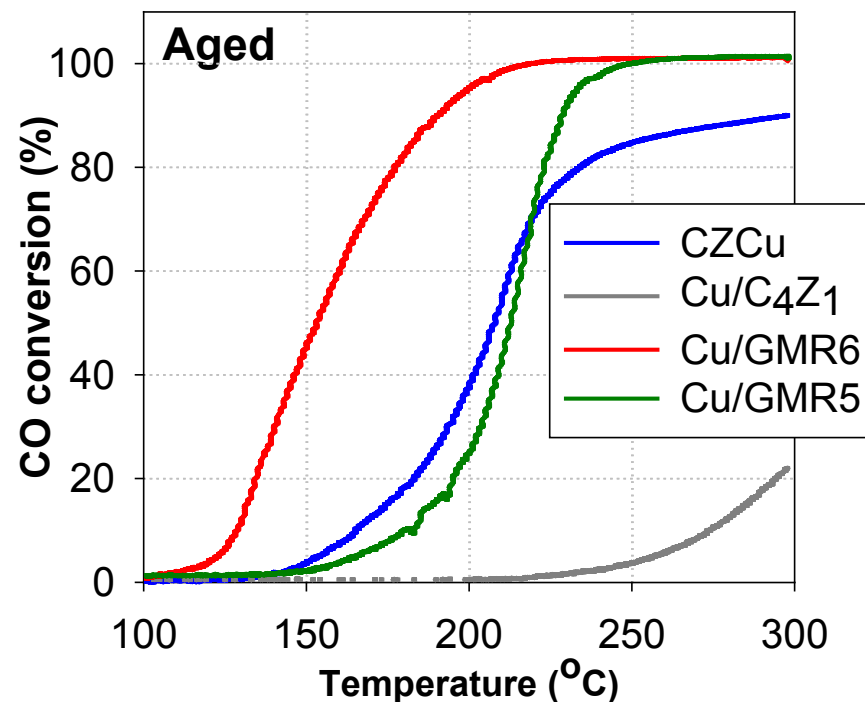
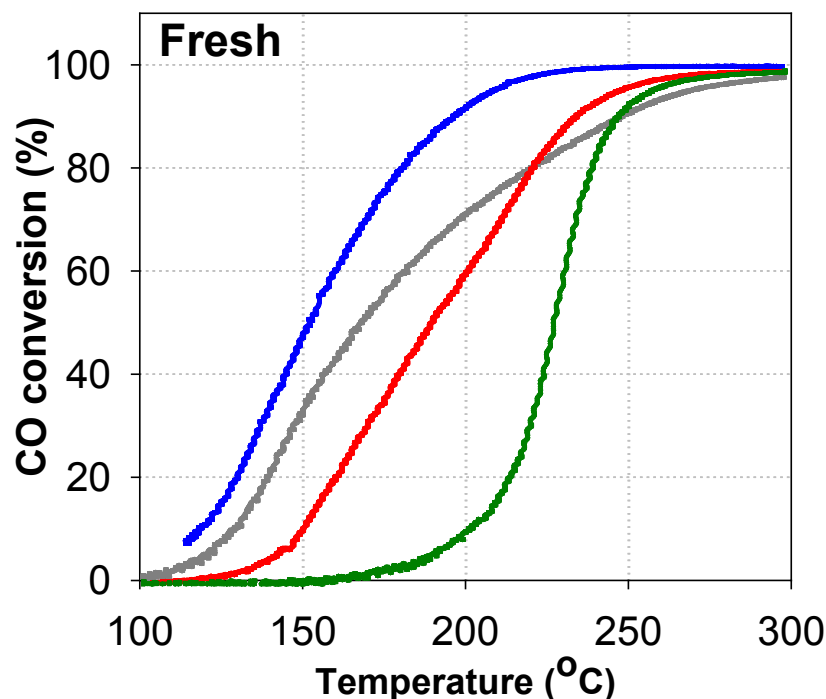
PNNL – Activity and Characterization

- catalyst structure and active sites
- alternative synthesis processes
- aging and poisoning

Approach

- ▶ Prepare and evaluate both fresh and lab-aged catalyst materials
- ▶ Utilize catalysis expertise, state-of-the-art analytical techniques and computational analysis to investigate:
 - Surface and bulk properties of the catalyst materials with respect to changes in composition and hydrothermal aging, poisoning:
 - XRD, XPS, TEM/EDS
 - Interaction between probe molecules (CO and NO) and the potential active sites
 - FTIR, MS, TPD, DFT
 - Alternative catalyst formulations

CO oxidation activities of CuO/CeZrO₂ catalysts (GM): *the effect of high temperature hydrothermal aging*



- **Most active fresh catalyst:** **CZCu** (prepared by coprecipitation), followed **Cu/C₄Z₁** (prepared by impregnation), and the two CuO catalysts on commercial, doped CeZrO₂ catalysts (**GMR5** and **GMR6**)
- **Hydrothermal aging:** dramatic drop in CO oxidation activity on all CuO catalysts on home-made supports; remarkable activity gain on CuO/GMR6.

[Feed composition: 500 ppm CO, 260 ppm C₃H₆, 87 ppm C₃H₈, 200 ppm NO, 8% O₂, 8% H₂O and N₂ balance. GHSV=170,000 h⁻¹. Catalyst aging: 750 °C for 72 h in 10% H₂O/air.]



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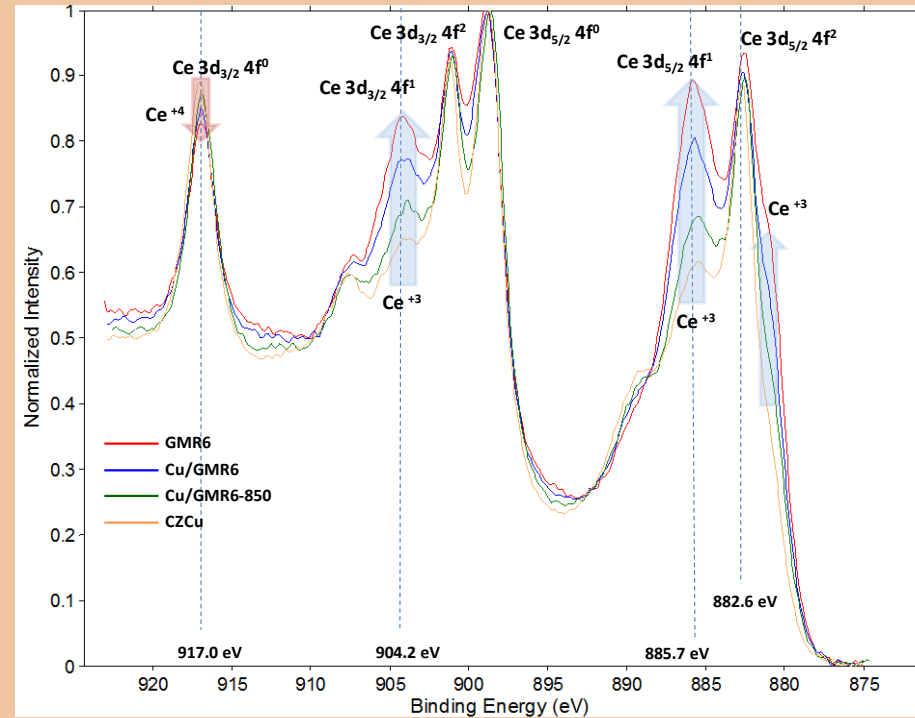
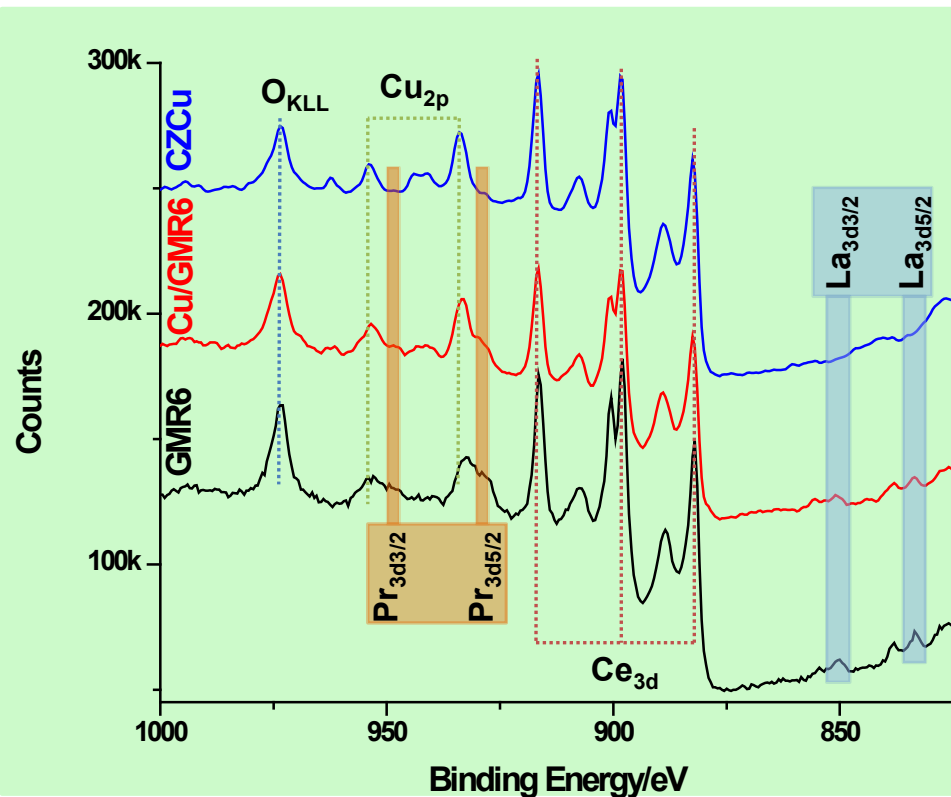
Deactivation: surface area of support and CuO particle size

Sample	Surface Area (m ² /g)		Area loss ^a	CuO crystallite size (nm) ^b	
	Fresh	Aged	%	Fresh	Aged
C4Z1	171	59	65.5	-	-
GMR5	83	77	7.2	-	-
GMR6	66	59	10.6	-	-
CZCu	123	6	95.1	7	24
Cu/C4Z1	122	0.4	99.7	6	27
Cu/GMR6	53	30	43.4	8	11

^a Surface Area loss calculated by $(S_{\text{fresh}} - S_{\text{aged}}) / S_{\text{fresh}}$, ^b CuO crystallite size determined by XRD using the Sherrer equation.

1. Home made CeZrO₂ supports suffer huge loss of surface are.
2. Surface area loss of commercial CeZrO₂ supports is much less extensive.
3. CuO accelerates the loss of support surface area.
4. CuO particles severely agglomerate when supported on an home-made CeZrO₂.
5. Commercial CeZrO₂ supports preserve high CuO dispersion.

XPS: composition and reducibility of support



Commercial GMR6 support contains both La and Pr.

La: structural stabilizer

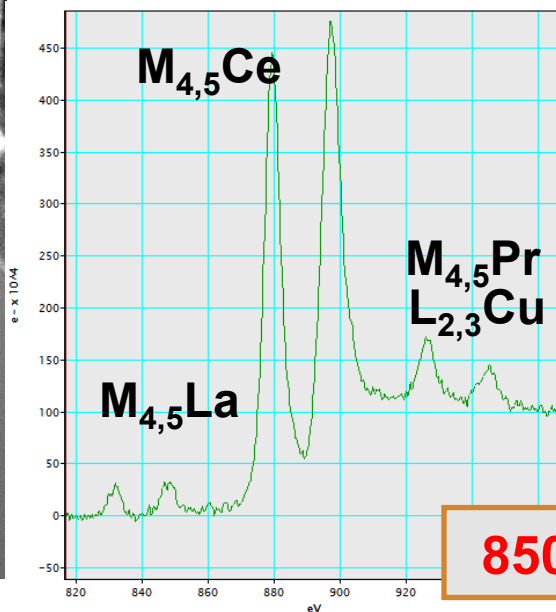
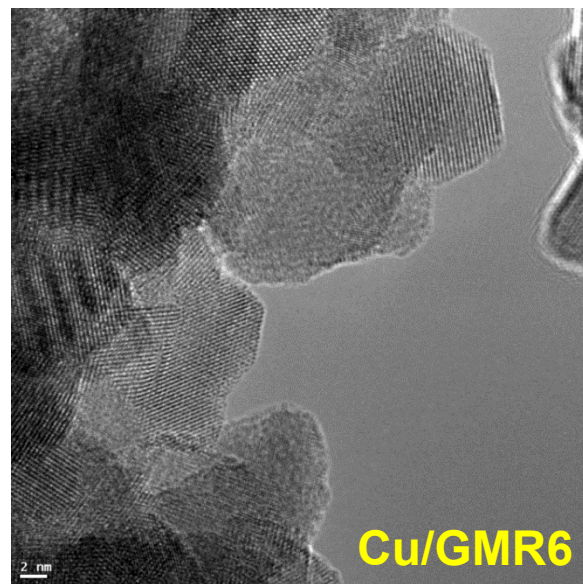
Pr: increase oxygen mobility

Highest extent of reducibility: commercial $CeZrO_2$ support (GMR6).

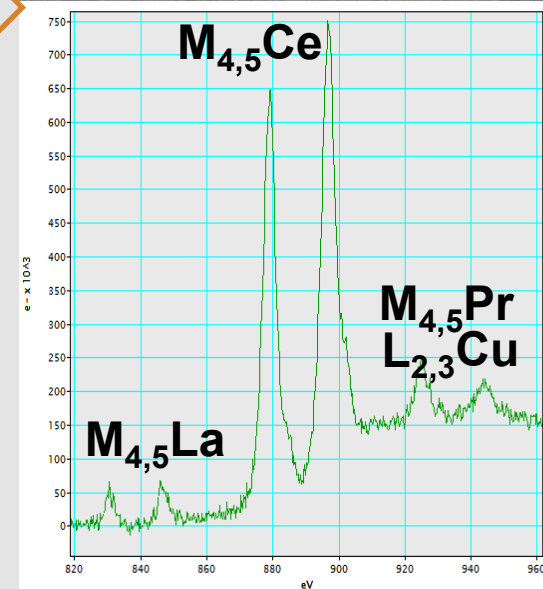
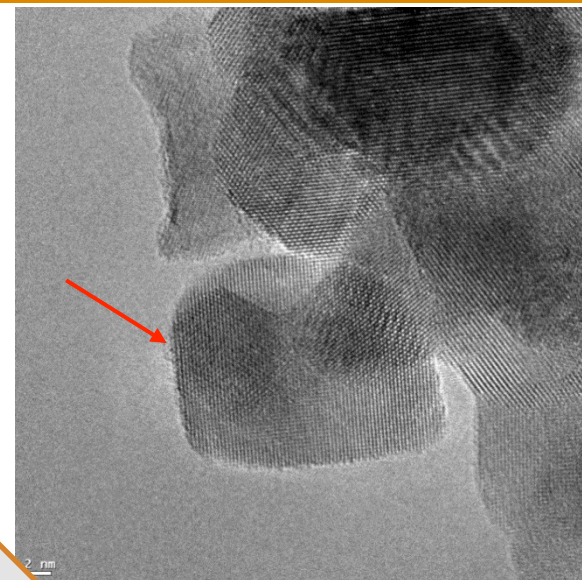
Addition of Cu: decrease the reducibility of the support material.

Higher reducibility may contribute to higher CO oxidation activity.

TEM/EDS of fresh and aged Cu/GMR6

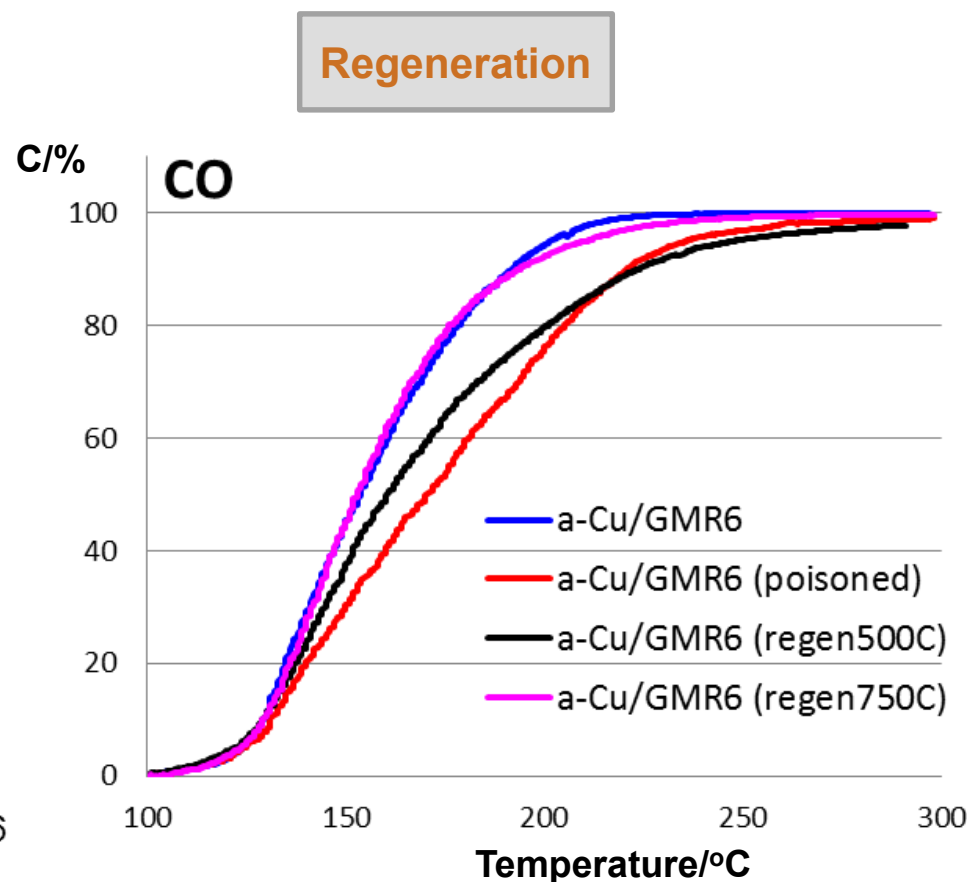
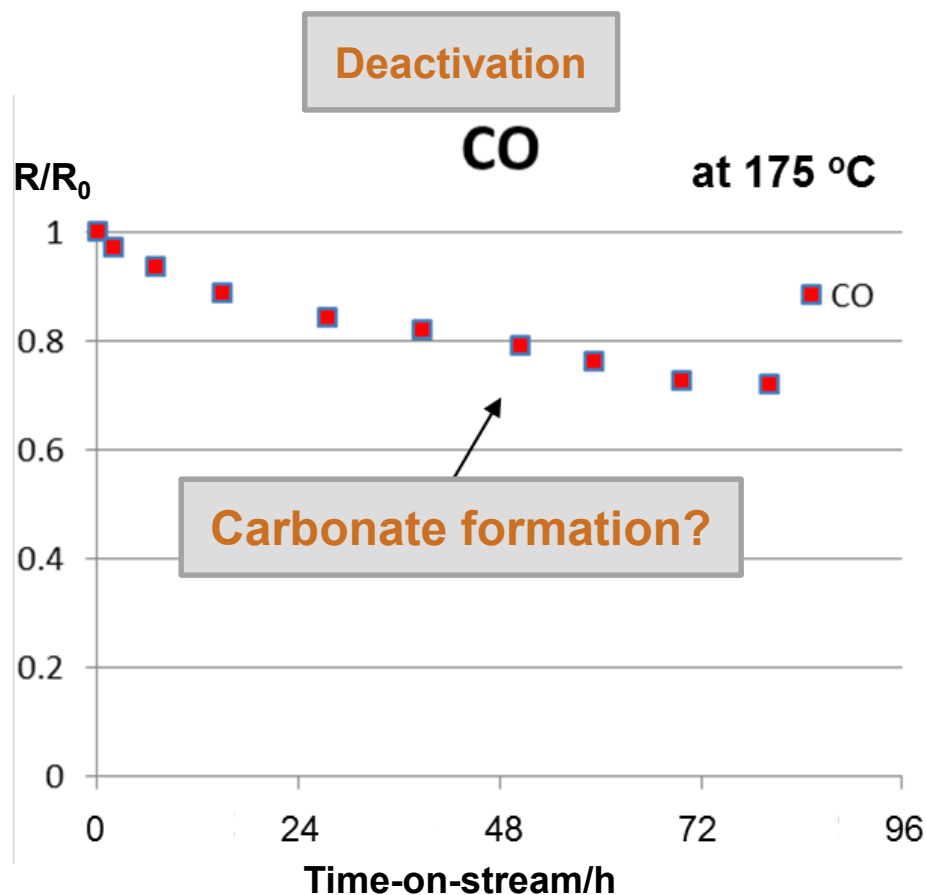


850 °C



1. Highly crystalline support and well dispersed CuO on both fresh and HT aged catalysts.
2. Uniform promoter (La and Pr) dispersion throughout the support

Catalyst deactivation and regeneration



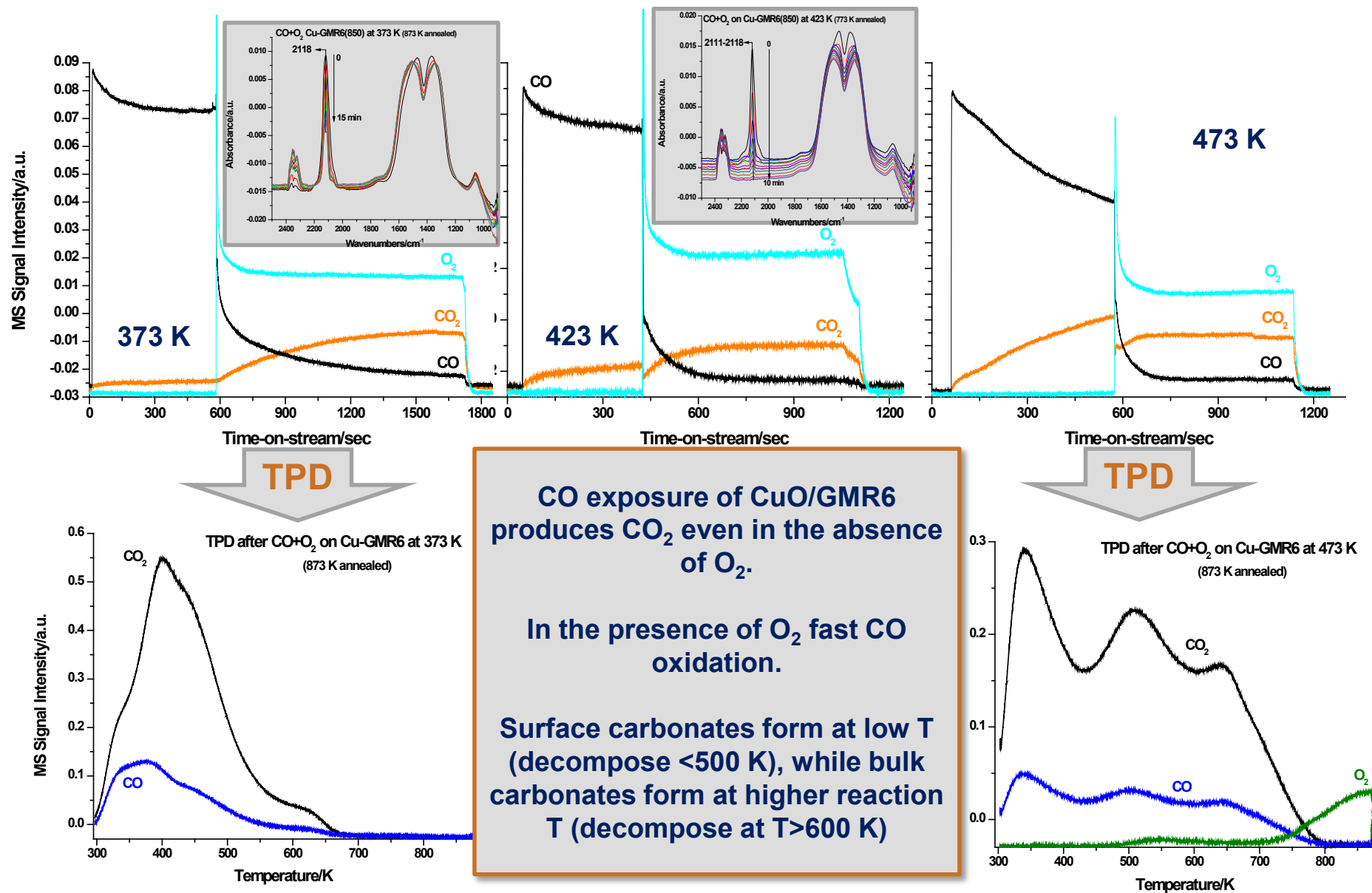
Slow, but steady deactivation at 175 °C.
Regeneration:
T < 500 °C: partial T > 750 °C: complete
carbonate accumulation is the source of deactivation



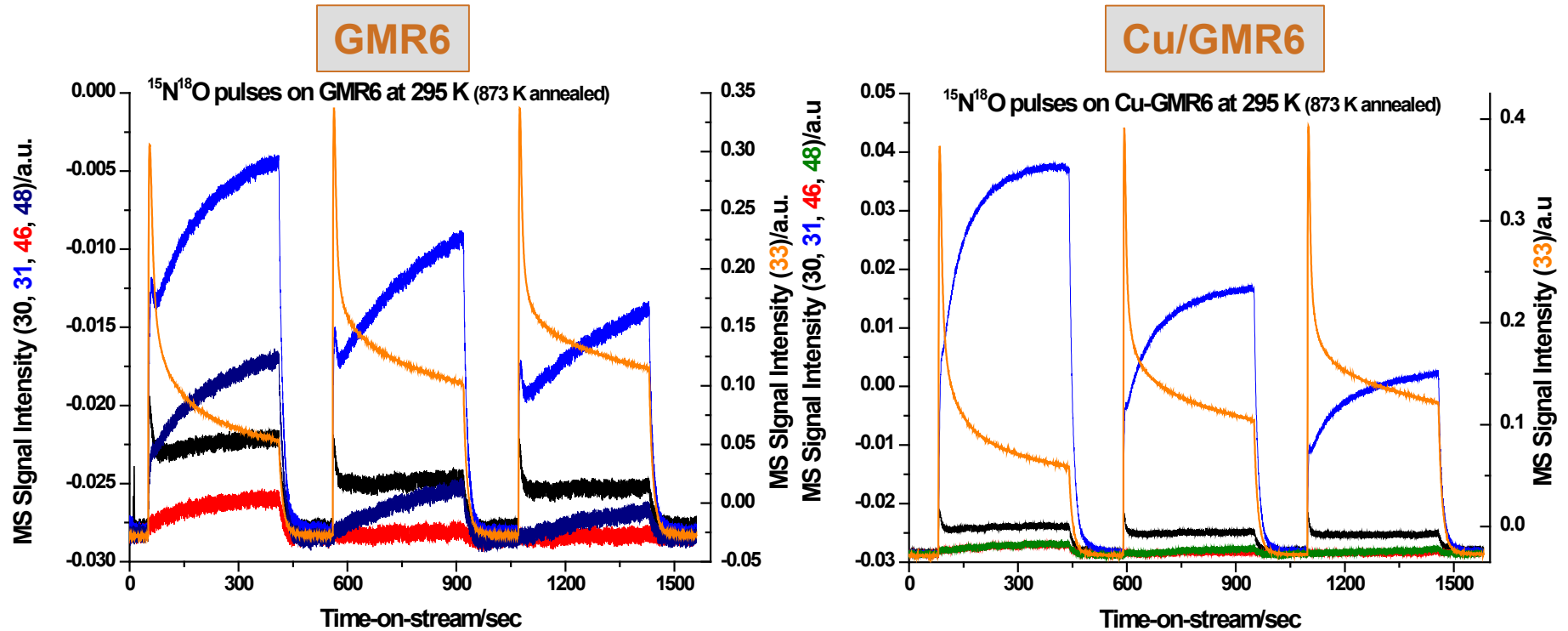
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CO and CO+O₂ on CuO/GMR6



Oxygen mobility followed by $^{15}\text{N}^{18}\text{O} \rightarrow ^{15}\text{N}^{16}\text{O}$ isotope exchange process on GMR6 and Cu/GMR6 at 295 K



Fast surface reaction:

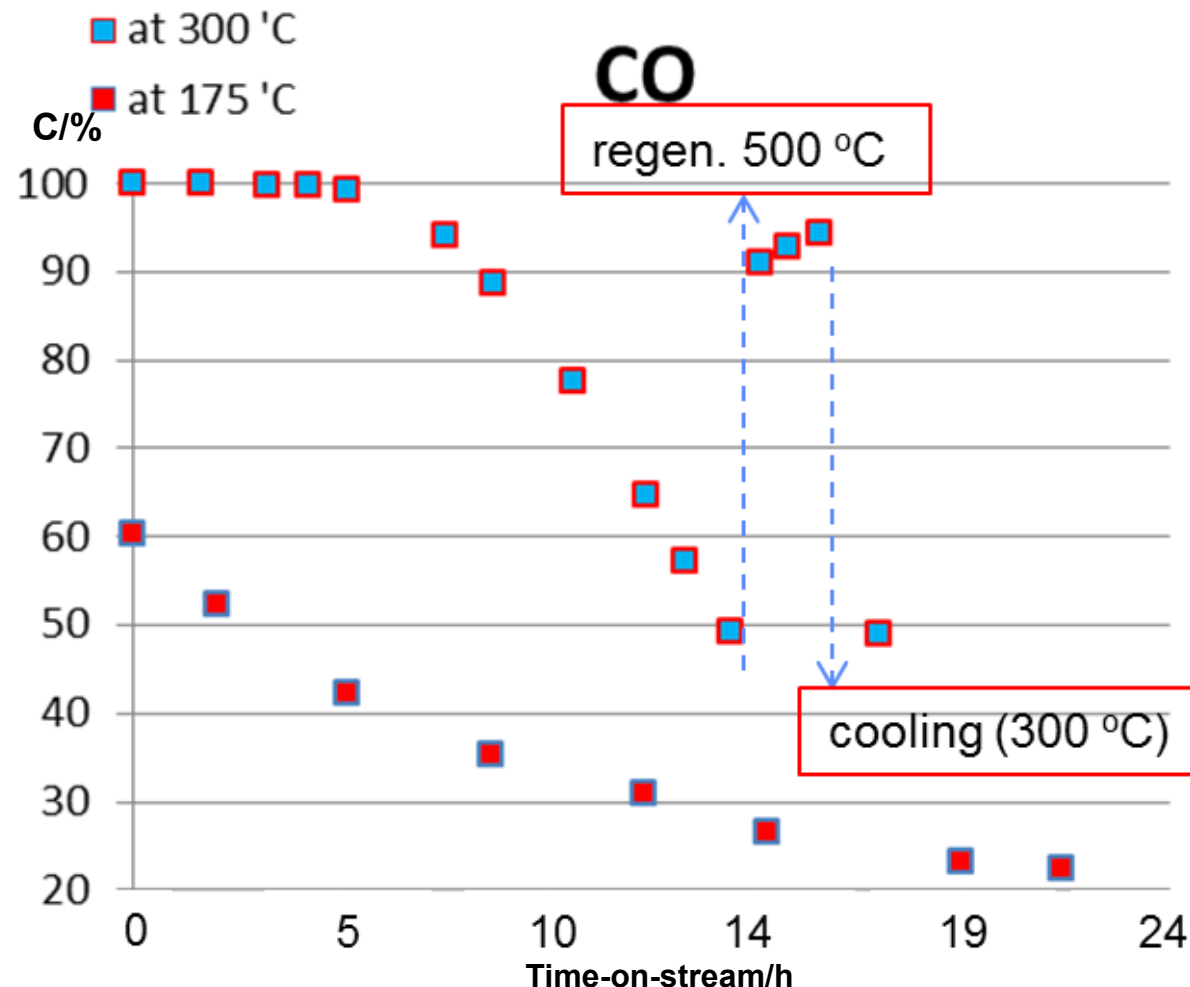


Besides $^{18}\text{O} \rightarrow ^{16}\text{O}$ isotope exchange NO reduction to N_2O and N_2 are also observed.

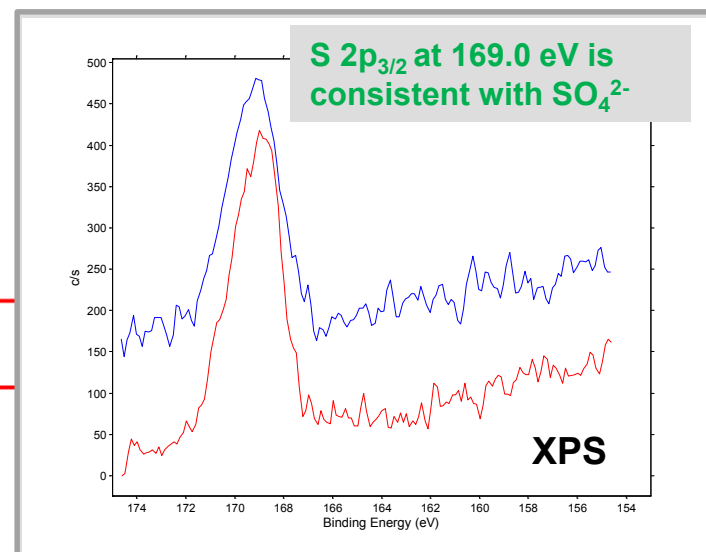
Much faster isotope exchange in the presence of CuO on GMR6:

very high oxygen mobility in Cu/GMR6

S poisoning and regeneration: Cu/GMR6



Feed: 500 ppm CO, 260 ppm C₃H₆, 87 ppm C₃H₈, 200 ppm NO, 8% O₂, 8% H₂O and N₂bal.
SO₂: 1 ppm for 21 hr at 175 °C (≈ 1.5 g_{SO₂}/L_{monolith}),
1 ppm for 14 hr at 300 °C (≈ 1.0 g_{SO₂}/L_{monolith})
Flow rate: 300 sccm, GHSV=170,000 h⁻¹
Temperature on stream: 175 °C and 300 °C
Regeneration: 500 & 750 °C for 2 h under feed condition w/o SO₂



Severe deactivation under both 175 °C and 300 °C.
Partial regeneration at T < 500 °C
Sulfate accumulation is the source of deactivation

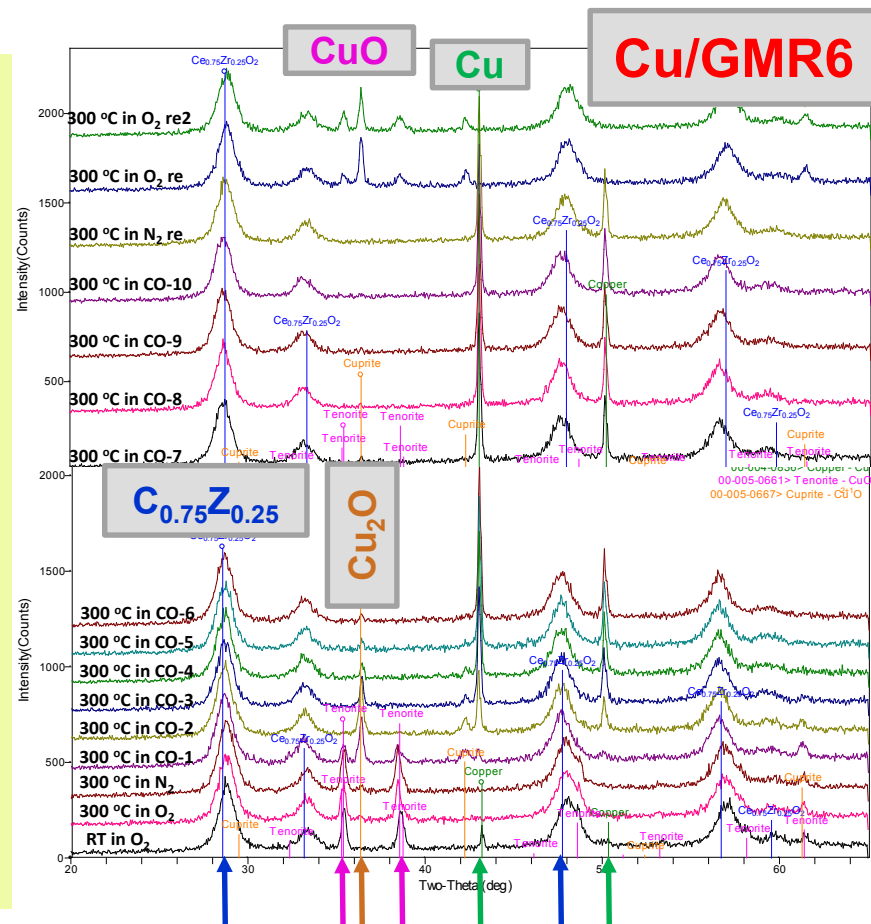
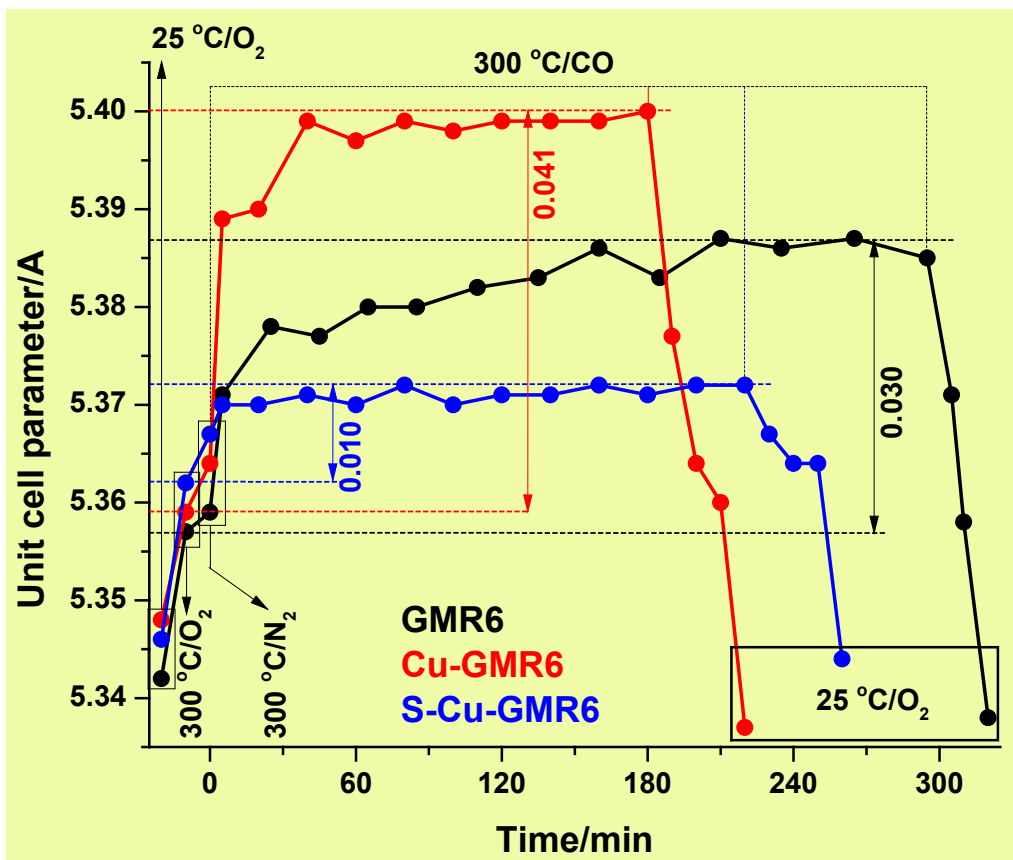


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Unit cell expansion upon reduction with CO: *the effect of S poisoning*



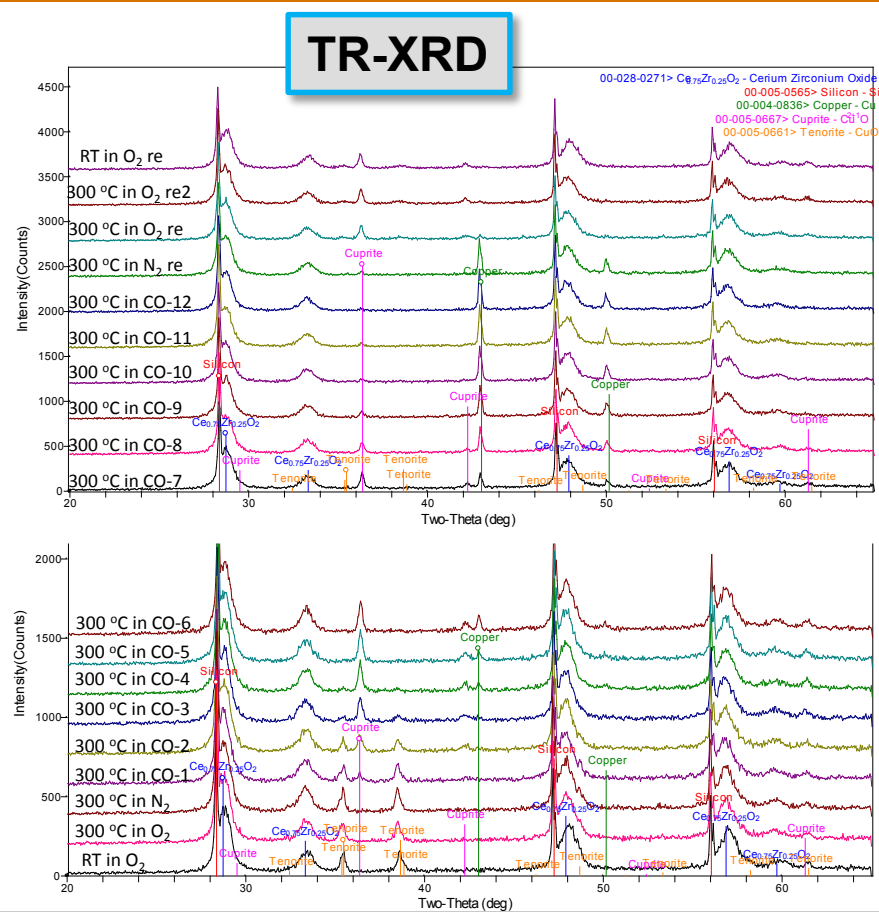
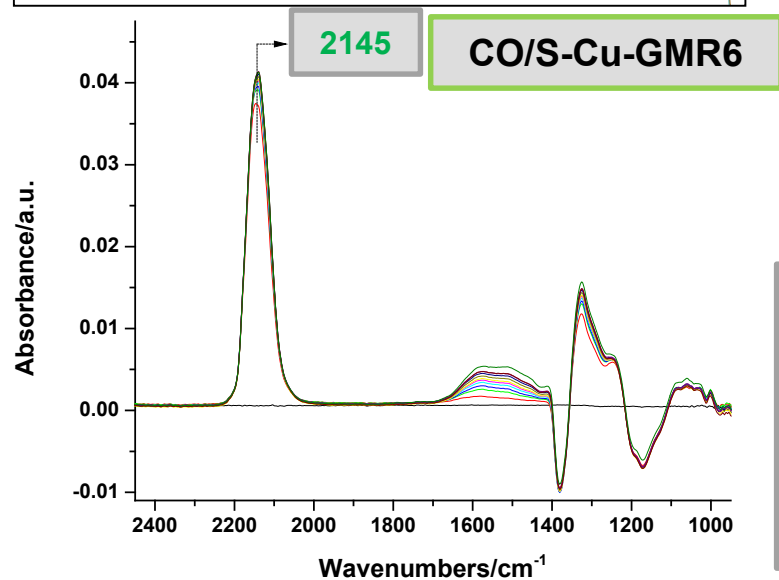
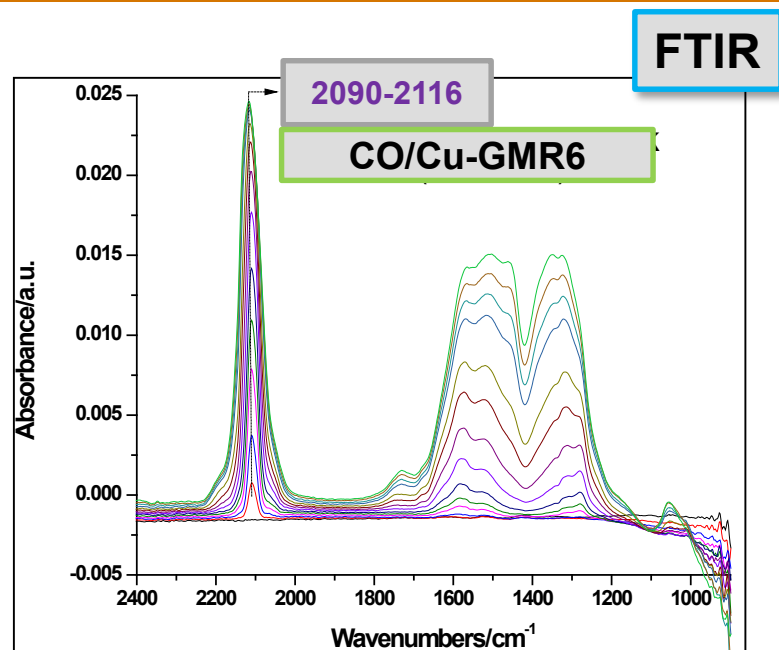
The exposure of Cu/GMR6 to CO at 300 °C leads to CO oxidation by labile lattice oxygen and the expansion of the CeZrO₂ lattice.

Highest level of reduction: Cu/GMR6

Lowest extent of reduction: S-poisoned Cu/GMR6

surface sulfates decrease the number of labile lattice oxygens available for CO oxidation.

S poisoning of Cu/GMR6

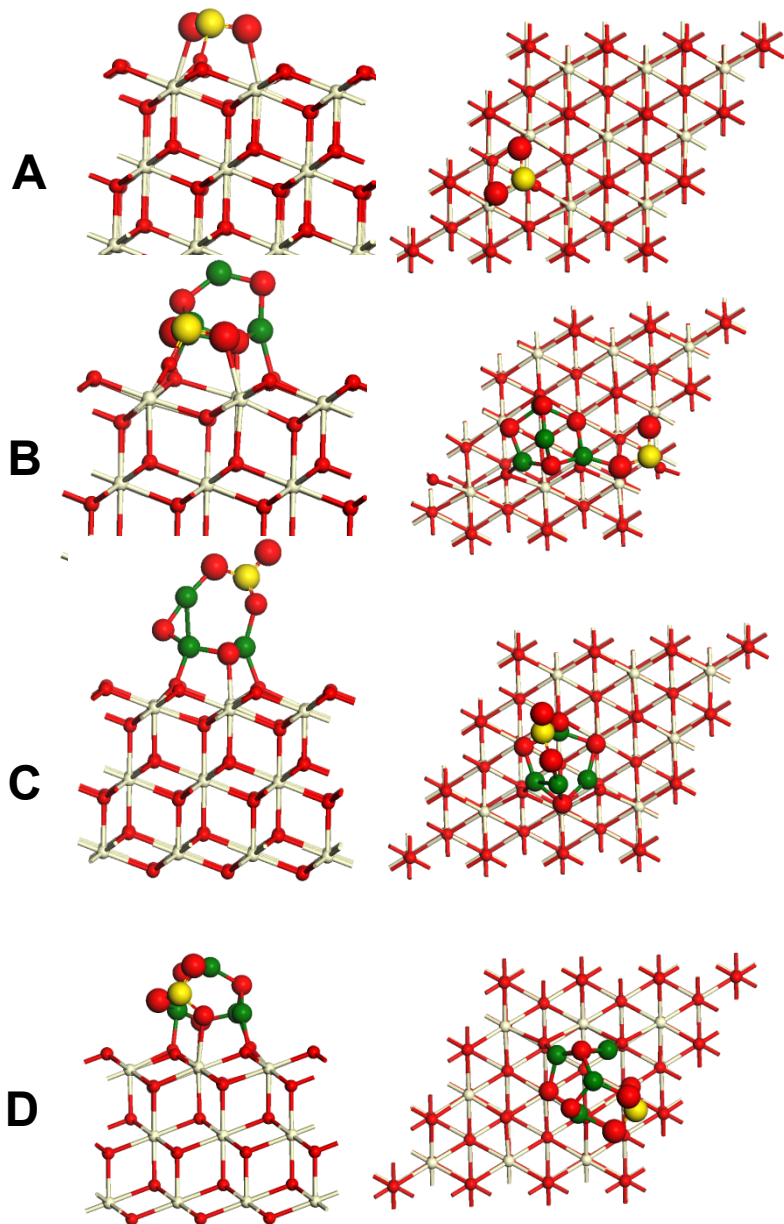


$\nu(\text{C-O})$ of $\text{CO}_{\text{ads}}/\text{S-Cu-GMR6} > \nu(\text{C-O})$ of $\text{CO}_{\text{ads}}/\text{Cu-GMR6}$

After S poisoning Cu is present as CuO, and can be reduced by CO the same way as in Cu/GMR6:

S mainly affects the GMR6 support

SO₂ adsorption on the (CuO)₄/CeO₂ surfaces



A	CeO ₂ (111)	CeO ₂ (100)	CeO ₂ (110)
	-0.97	-2.34	-1.95
	-1.68	-2.76	-2.10
CB	-1.27	-2.30	-2.64
D	-1.77	-2.40	-3.03

SO₂ adsorption on the CeO₂(100) and CeO₂(110) surfaces are stronger. With the (CuO)₄ cluster, SO₂ adsorption on the CeO₂ surfaces becomes stronger.

On the (CuO)₄/CeO₂ surfaces, SO₂ prefers to adsorb at the surface and interface instead of the cluster:

modifies CO adsorption properties of the cluster
and
reduces oxygen mobility of the support

Light-off temperature for CO oxidation

Catalyst	T _{50%} (°C)
CuO-GMR6	157
1%CuO-GMR6	173
5%CuO-GMR6	160
10%CuO-GMR6	160
10%CuO-HTA-GMR6	178
HTA-10%CuO-GMR6	145
HTA-10%CuO-HTA-GMR6	148
20%CuO-GMR6	164
5%CuO-CeO₂ (rods)	130
10%CuO-CeO₂ (rods)	133
10%CuO-HTA-CeO ₂ (rods)	207
5%CuO-CeO ₂ (cubes)	159
5%Co ₃ O ₄ -CeO ₂ (cubes)	246
5%Co ₃ O ₄ -CeO ₂ (rods)	248
1%Mn ₂ O ₃ -CeO ₂ (NP)	204
5%Mn ₂ O ₃ -CeO ₂ (NP)	278
10%Mn ₂ O ₃ -CeO ₂ (NP)	305
5%CuO-1%Mn ₂ O ₃ -CeO ₂ (NP)	172
5%CuO-5%Mn ₂ O ₃ -CeO ₂ (NP)	162
5%CuO-10%Mn ₂ O ₃ -CeO ₂ (NP)	182
10%Cu-CeO₂/ZrO₂	136
10%Cu-HTA-CeO ₂ /ZrO ₂	173
10%Cu-1.75%La₂O₃-CeO₂/ZrO₂	135
10%Cu-10%La₂O₃-CeO₂/ZrO₂	135

HTA – High Temperature Hydrothermal Aging.

Summary of “new” catalysts tested

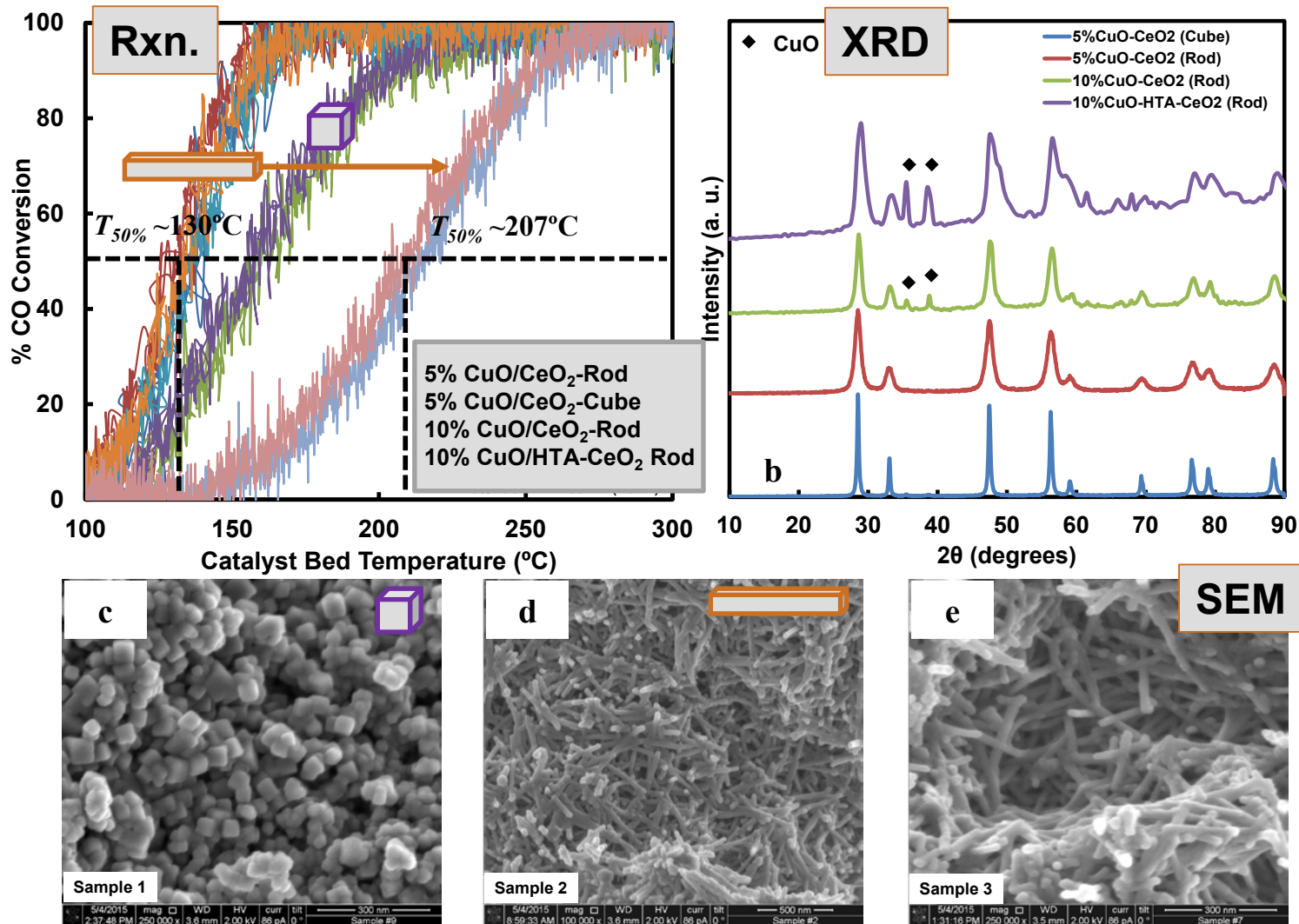
HTA of Cu/GMR6 improves catalytic activity toward CO oxidation.
HTA of Cu/GMR6 ≠ Cu/HTA-GMR6

CuO nanorods on GMR6 is more catalytically active than CuO nanocubes
Both nanorods and nanocubes loose their activities upon HTA

Neither Co₃O₄ nor Mn₂O₃ are effective CO oxidation catalysts on CeO₂.

High CO oxidation activity on both ZrO₂ and La₂O₃ doped CeO₂.
The addition of ZrO₂ (and La₂O₃) stabilizes the CeO₂ during HTA.

The effect of support morphology CuO/CeO₂: *rod vs. cube* (the role of crystal facets)



CuO on rod-shaped CeO₂ shows higher CO oxidation activity than on cube-shaped support.
Neither rods nor cubes are hydrothermally stable.

Future Plan

Complete activity measurements on C₁₂ hydrocarbon oxidation over selected (mostly GMR6-based) CuO catalysts.

Complete mechanistic DRIFTS studies on selected catalysts.

Complete two manuscripts based on work done at GM and PNNL.

Complete Final Report.

Summary

All CuO/CeO₂-based catalysts prepared by GM and PNNL showed high CO oxidation, but modest C₃ hydrocarbon oxidation activities. (... but not Co₂O₃ and Mn₂O₃)

All the home-made, CeO₂-based support materials showed poor high temperature hydrothermal stabilities (large increase in T_{50%}, large drop in surface area, agglomeration of active catalytic phase).

GMR6, a commercial La₂O₃- and Pr₂O₃-doped CeZrO₂ support showed remarkable high temperature hydrothermal stability (CO oxidation activity of HTA-Cu/GMR6 > Cu/GMR6).

La₂O₃ and ZrO₂ significantly enhance the hydrothermal stability of CeO₂.

Pr₂O₃ improves oxygen mobility on CeO₂.

Two reason for activity loss in Cu/GMR6: (1) surface and bulk carbonate formation (completely reversible by HT annealing/calcination), and (2) sulfate formation on the support and at the active oxide/support interface (only partially reversible).

Maintenance of high oxygen mobility in the CeO₂-based support is key to long term high CO oxidation activity (Mars-van-Krevelen mechanism).

TECHNICAL BACKUP

Supplementary slide:

Alternative catalysts: support, additive, active oxide

Catalyst	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)
CeO ₂ (C)	34.2	0.27	32.2
CeO ₂ (R)	129.5	0.89	27.4
5%CuO-CeO ₂ (C)	32.8	0.21	25.1
5%CuO-CeO ₂ (R)	115.2	0.52	18.1
5%Co ₃ O ₄ -CeO ₂ (C)	30.6	0.01	12.7
5%Co ₃ O ₄ -CeO ₂ (R)	81.4	0.16	7.8
Commercial CeO ₂	37.7	0.77	20.5
1%Mn ₂ O ₃ -CeO ₂	31.6	0.13	17.3
5%Mn ₂ O ₃ -CeO ₂	29.0	0.11	17.3
10%Mn ₂ O ₃ -CeO ₂	22.8	0.09	17.4

Catalyst	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)
GMR6	68.2	0.47	27.4
10%Cu-GMR6	58.9	0.21	14.4
10%Co-GMR6	54.8	0.22	16.1
HTA-GMR6	53.5	0.47	37.1
10%Cu-HTA-GMR6	42.8	0.23	21.6
10%Co-HTA-GMR6	41.9	0.21	19.9
HTA-10%Cu-GMR6	26.1	0.2	30.5
HTA-10%Co-GMR6	23.3	0.22	37.1
HTA-10%Cu-HTA-GMR6	27.0	0.23	33.8
HTA-10%Co-HTA-GMR6	22.3	0.2	36.0

CeO₂ support: rod and cube shaped: high initial activity; low hydrothermal stability

Co₃O₄/CeO₂: much lower activity than CuO/CeO₂

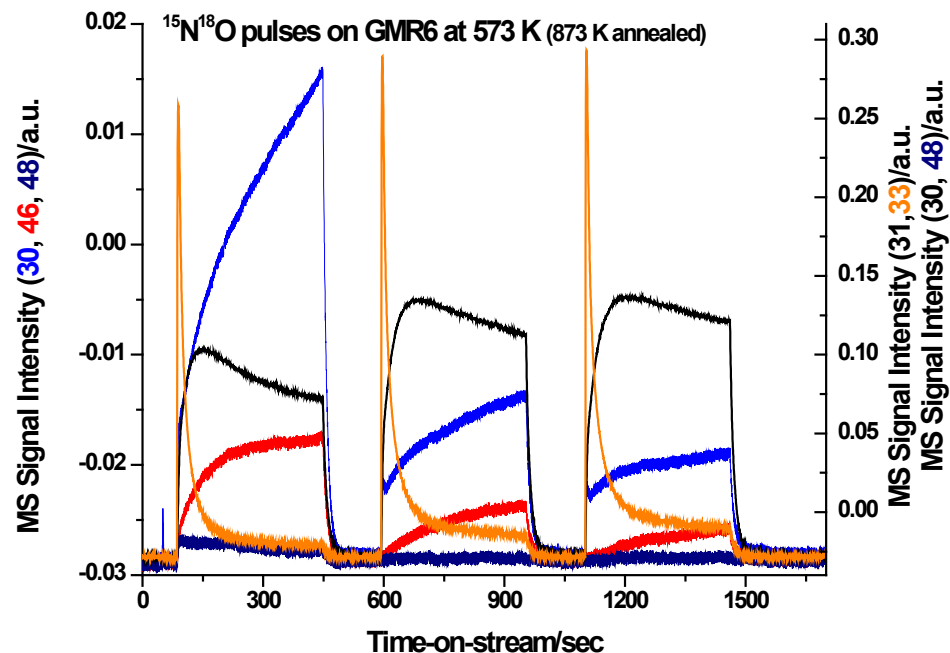
Mn₂O₃/CeO₂: much lower activity than CuO/CeO₂

GMR6 support shows high hydrothermal stability (both with CuO and Co₃O₄)

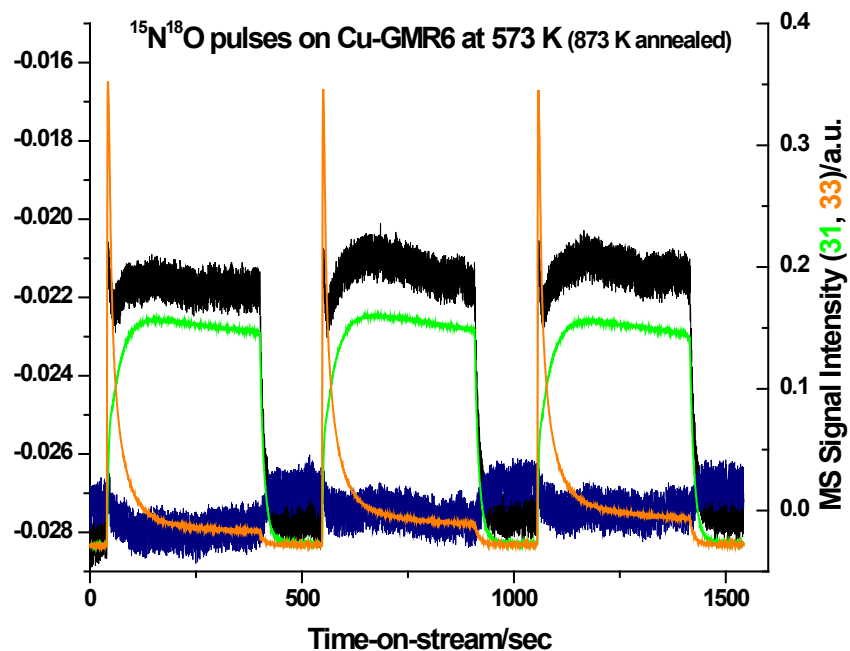
The best catalyst (both catalytic performance and hydrothermal stability) is CuO supported on GMR6. Non of the catalyst tested showed sufficient C₃ oxidation ability, but CuO/GMR6 was sufficiently active in C₁₂ oxidation.

Supplementary slide: $^{15}\text{N}^{18}\text{O}$ exposure of GMR6 and Cu/GMR6 at 573 K

GMR6

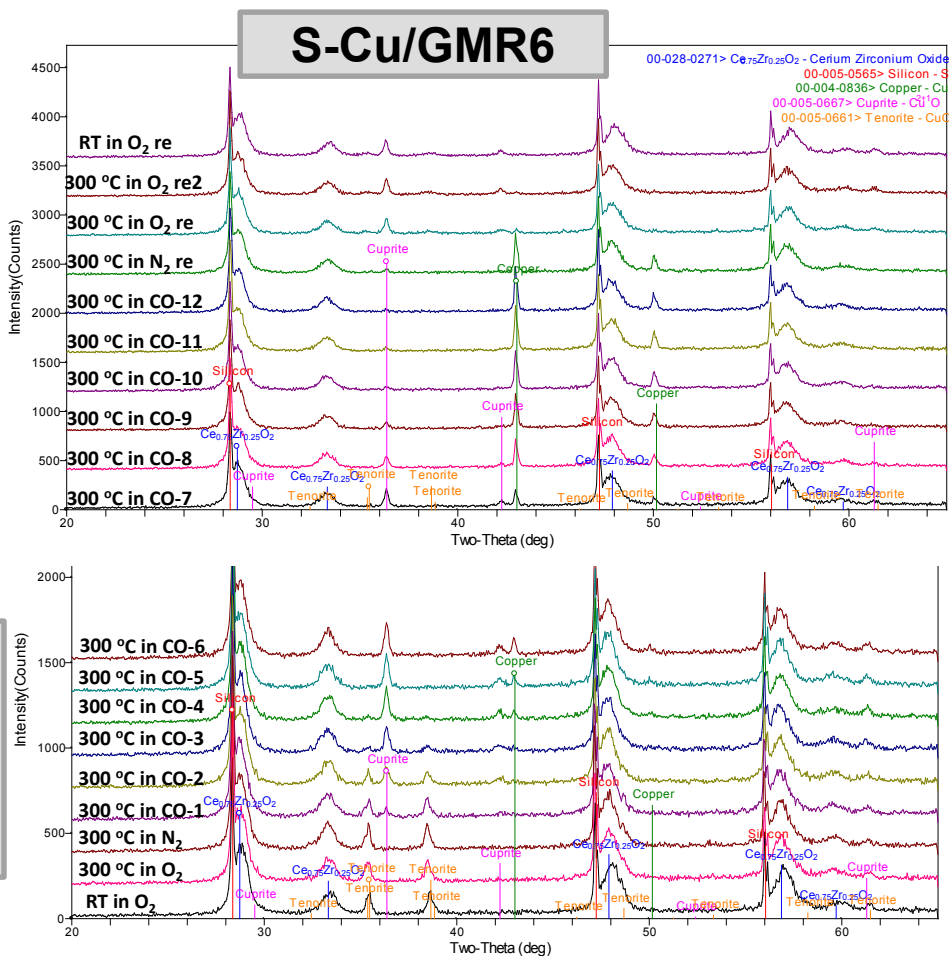
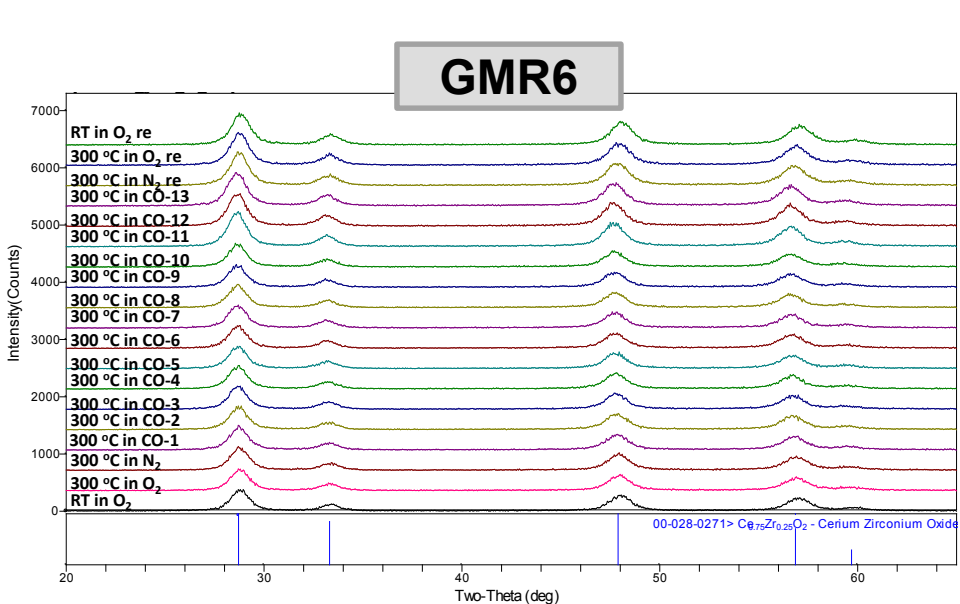


Cu/GMR6



Much faster rate of oxygen isotope exchange at 573 K than at 295 K.
Significant NO reduction to N_2O and N_2

Supplementary Slide: TR-XRD

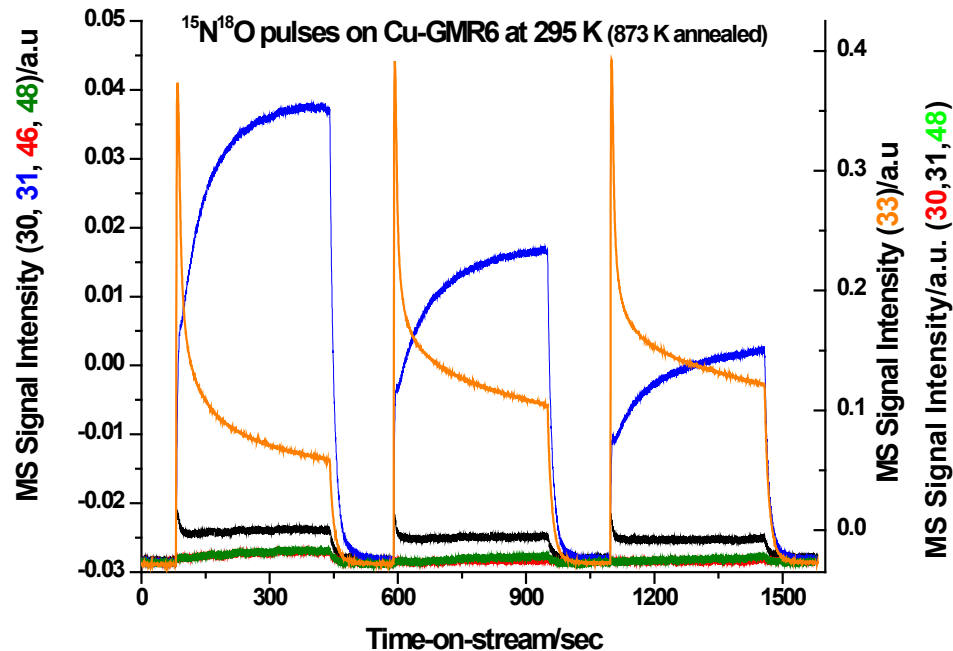


**Without Cu (CuO) the removal of lattice oxygen is slow.
 Cu(CuO) greatly enhances the rate of lattice oxygen reactivity**

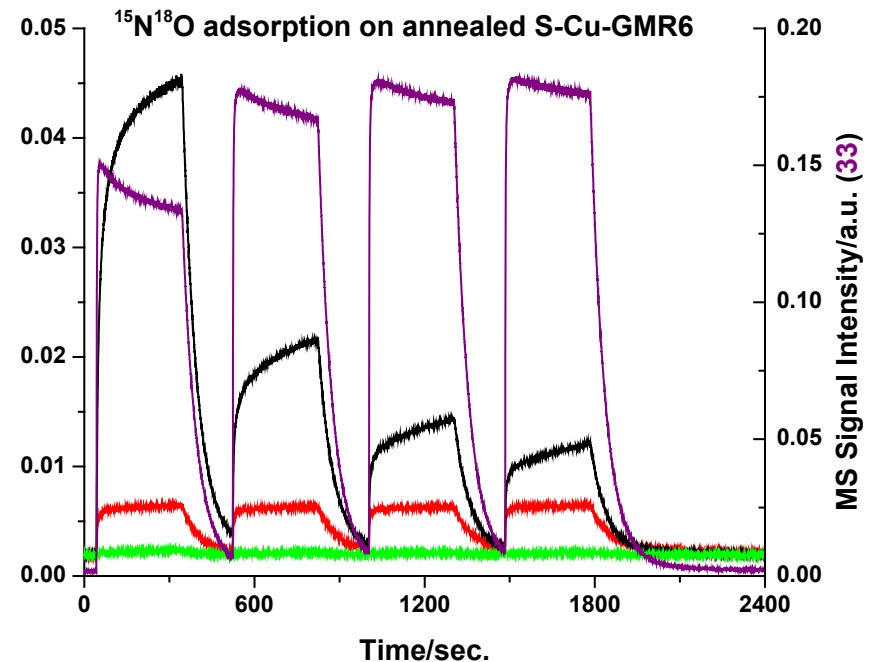
Sulfur poisoning affects both the support (GMR6) and the CuO phase. The formation of Cu_2O and then Cu is much slower on the S-poisoned sample than over the Cu-GMR6. Re-oxidation (after CO reduction) only results in the formation of Cu_2O but not CuO. Very small unit cell parameter decrease is seen for the S-poisoned GMR6 support.

Oxygen mobility: $^{15}\text{N}^{18}\text{O} \rightarrow ^{15}\text{N}^{16}\text{O}$ isotope exchange process on Cu/GMR6 and S-Cu/GMR6 at 295 K

Cu/GMR6



S-Cu/GMR6



Much faster surface reaction on Cu/GMR6 than on S-Cu/GMR6:

S poisoning dramatically decreases surface oxygen mobility

