

Investigation of Sulfur Deactivation on Cu/Zeolite SCR Catalysts in Diesel Application

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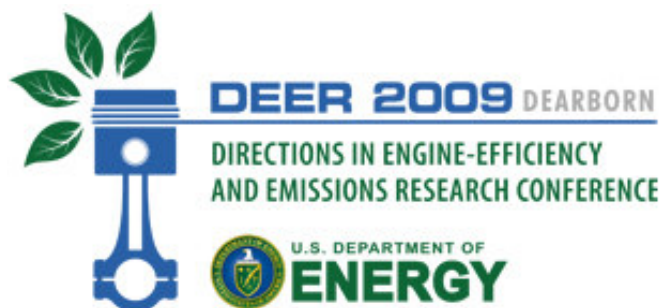
Ford Motor Company

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Pacific Northwest National Laboratory

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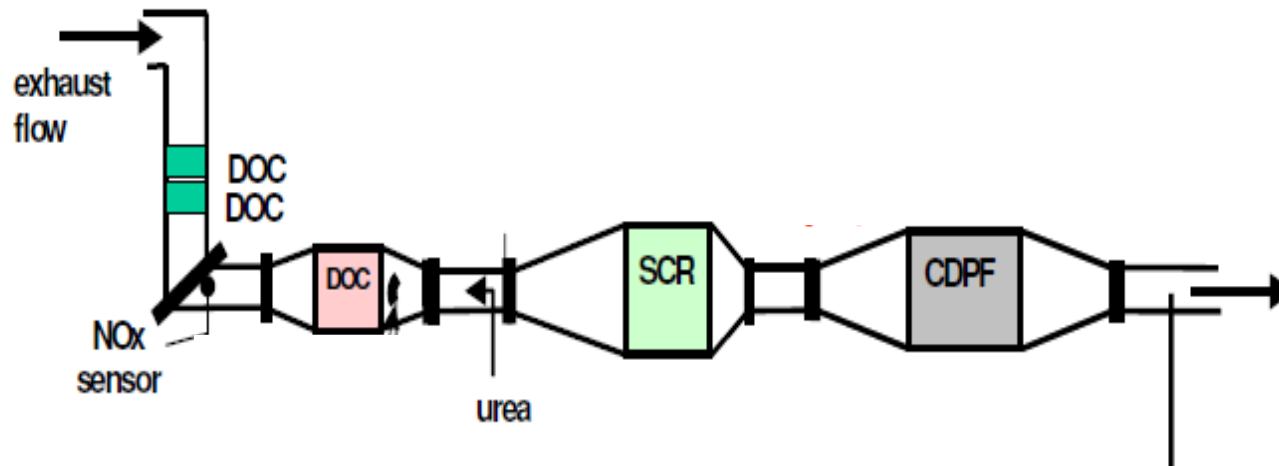
Urea SCR Catalysts in Diesel Application

- Cu, Fe Zeolite catalyst
- Leading candidate for treatment of NO_x emission for North America Diesel applications.
- Better options for Heavy-duty Diesel Engines
- Already commercialized in Europe
- **Durability issues:**
 - Dealumination and zeolite structure collapse due to hydrothermal aging at high temperature
 - Cu sintering due to the reducing agents
 - Poisonings: such as S, P, Zn



SO_x on Cu/zeolite SCR catalysts

- Sulfur poisoning is still a durability issue for base metal/zeolite SCR catalysts, especially for Cu/Zeolite SCR catalysts.
- Most studies have been based on SO₂.
- As DOCs are employed upstream of the SCR catalysts, it is likely that a portion of the SO₂ are oxidized into SO₃.
- Investigation of the impact of SO₃ on Cu/zeolite SCR catalysts is important.



Experimental

- Catalysts:
 - Fully formulated monolith Cu/zeolite.
 - Six (6) 1x1 samples.
- Procedure:
 - Hydrothermal aging at 670C for 20 hr.
 - S poisoning:
 - 40ppm for 1.5hr with SO₂ or SO₃ at
 - 200 °C, 300 °C, 400 °C
 - Total S throughput equivalent to 500 miles with 350ppm sulfur fuel
 - DeSO_x: 170 °C to 770 °C at 5 °C/min.
- Characterization:
 - XPS, Cu XAFS, Cu XANES



SCR Activity Testing Sequence

Hydrothermal Aging

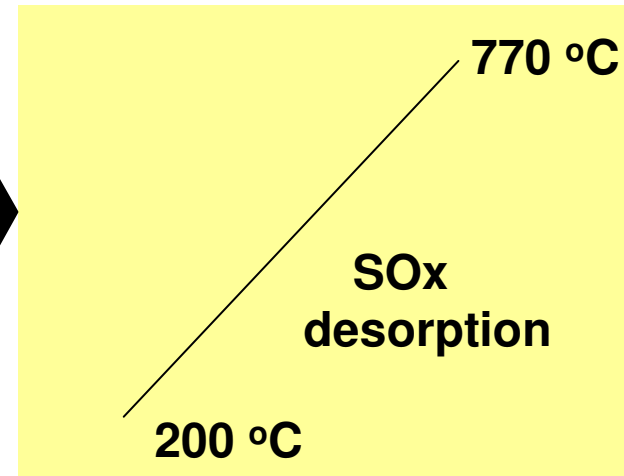
Test #1: Baseline

Sulfation with SO_2 or SO_3

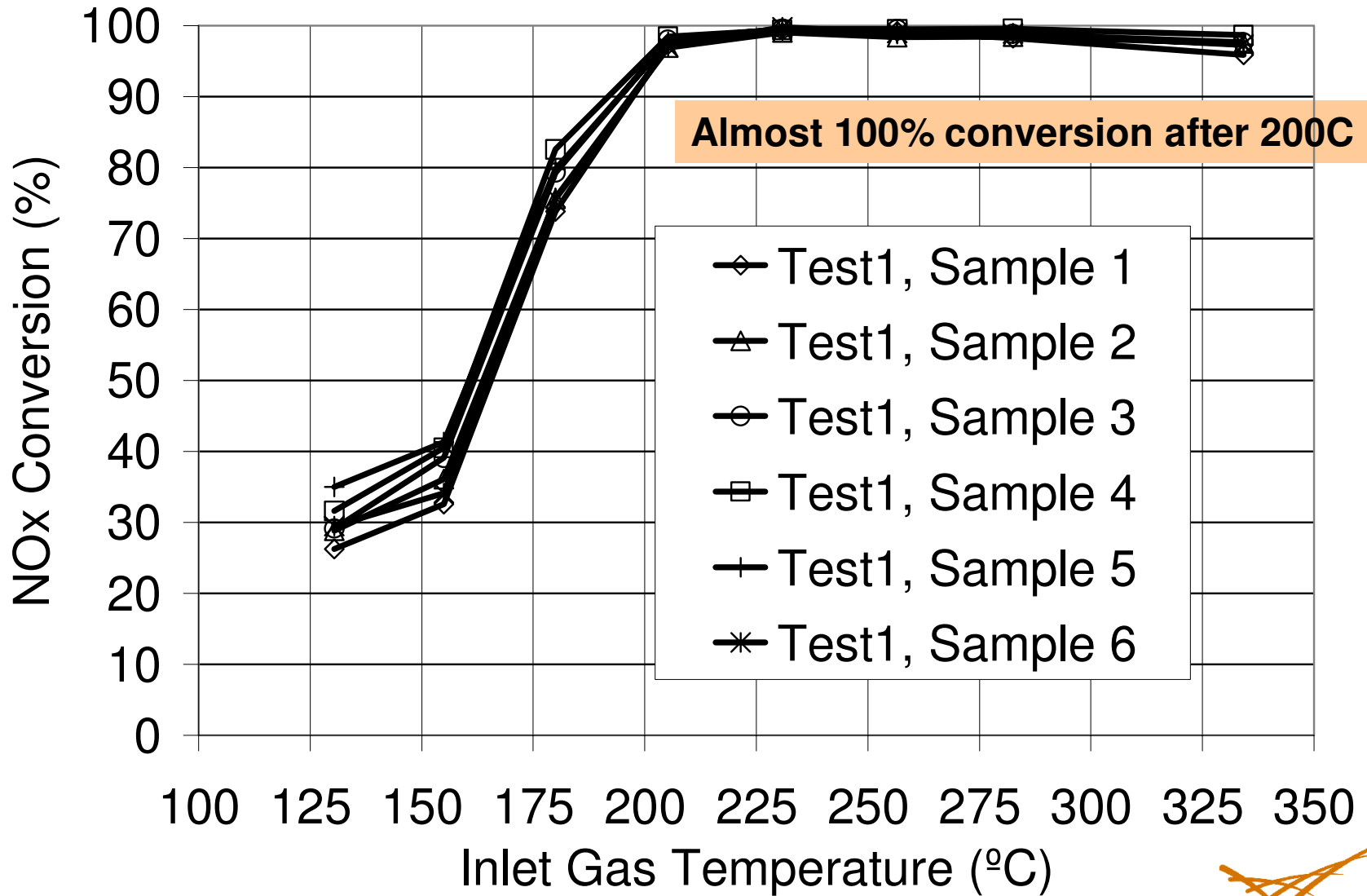
Test #2: Sulfation effect

De-Sulfation with O_2 , H_2O
and CO_2 up to 770°C : TPD

Test #3: De SO_x effect

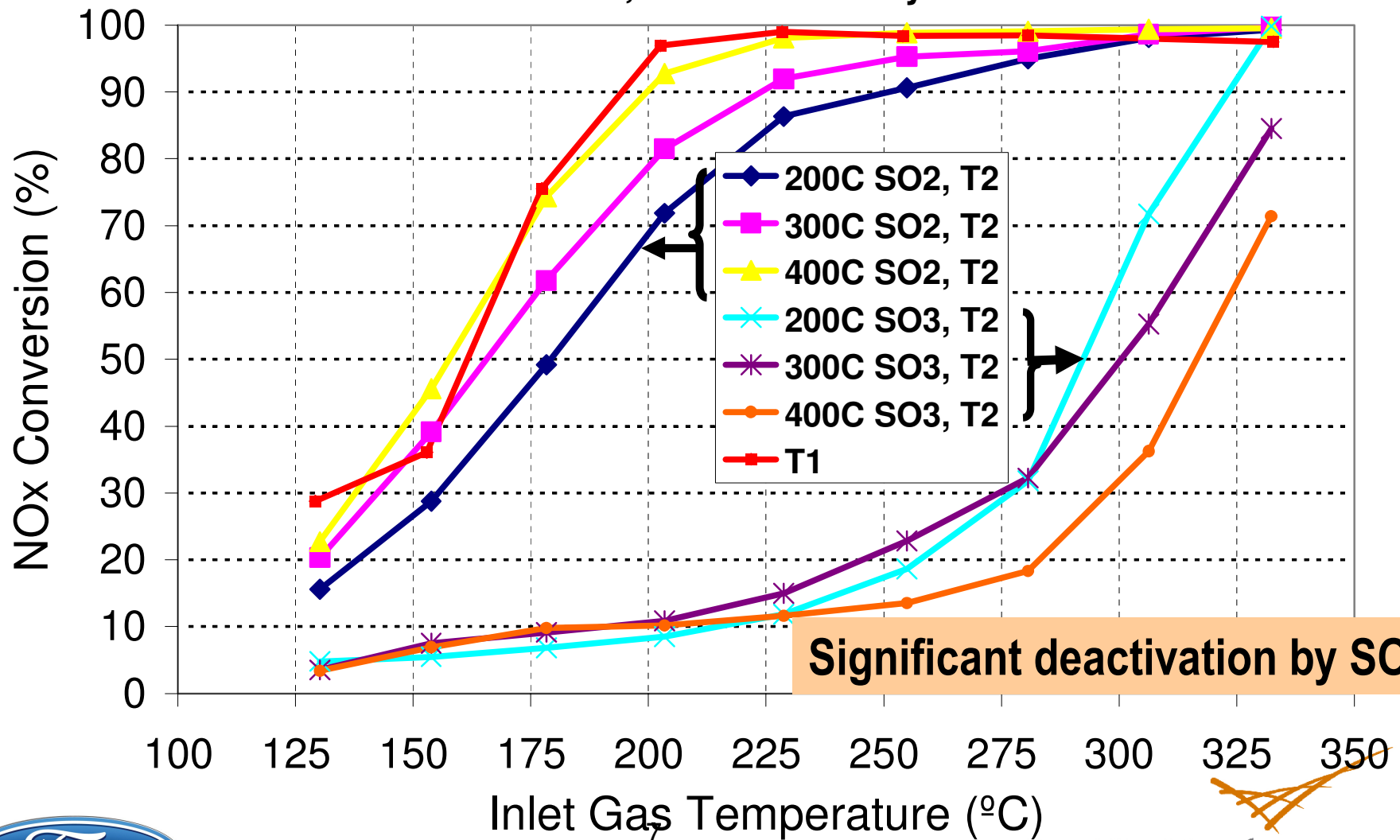


NOx Activity After Thermal Aging



SO₂ vs. SO₃ – The impacts on NO_x conversion

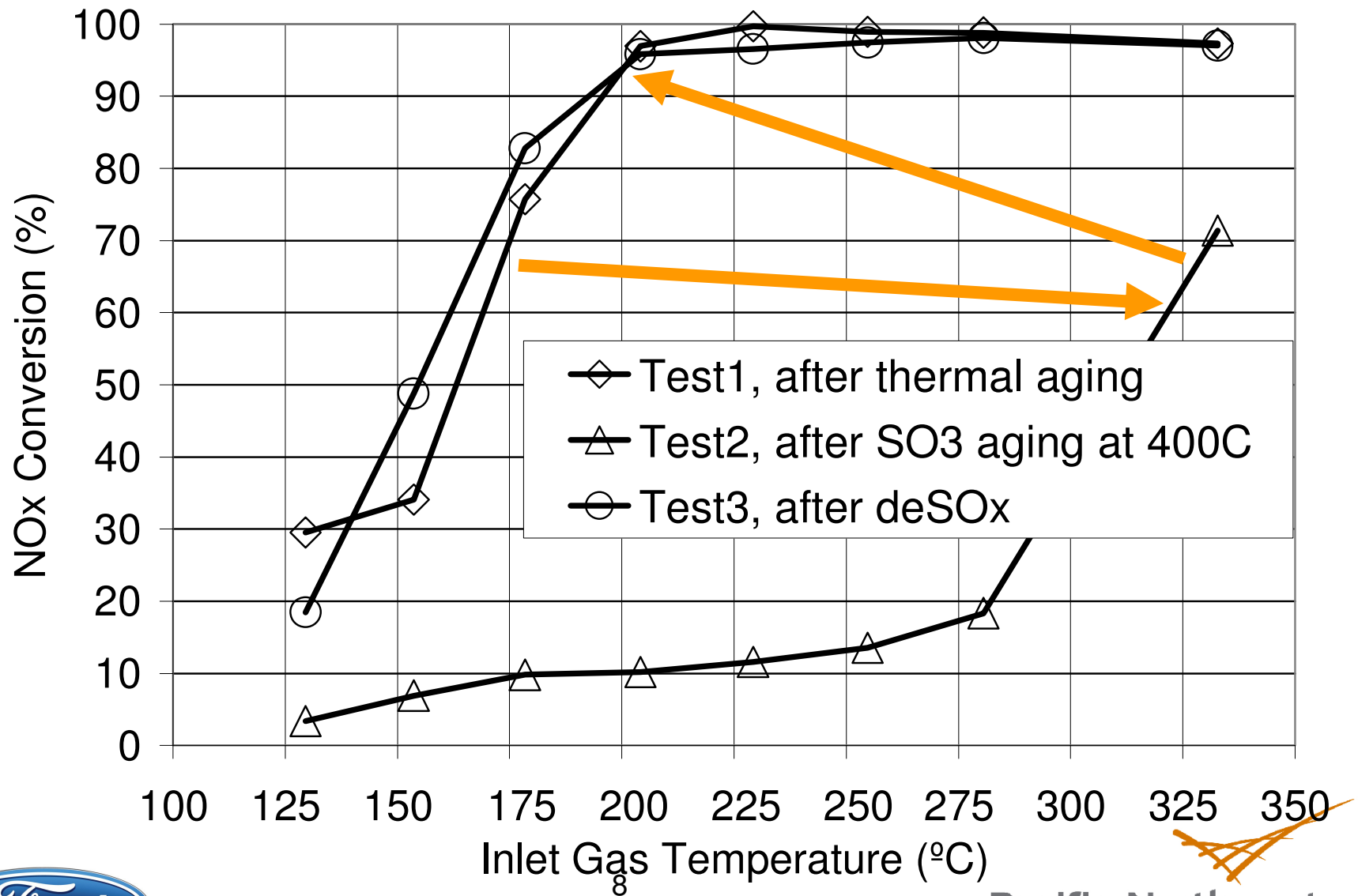
NO_x Conversion
SV = 30,000/hr - NO only



Significant deactivation by SO₃!

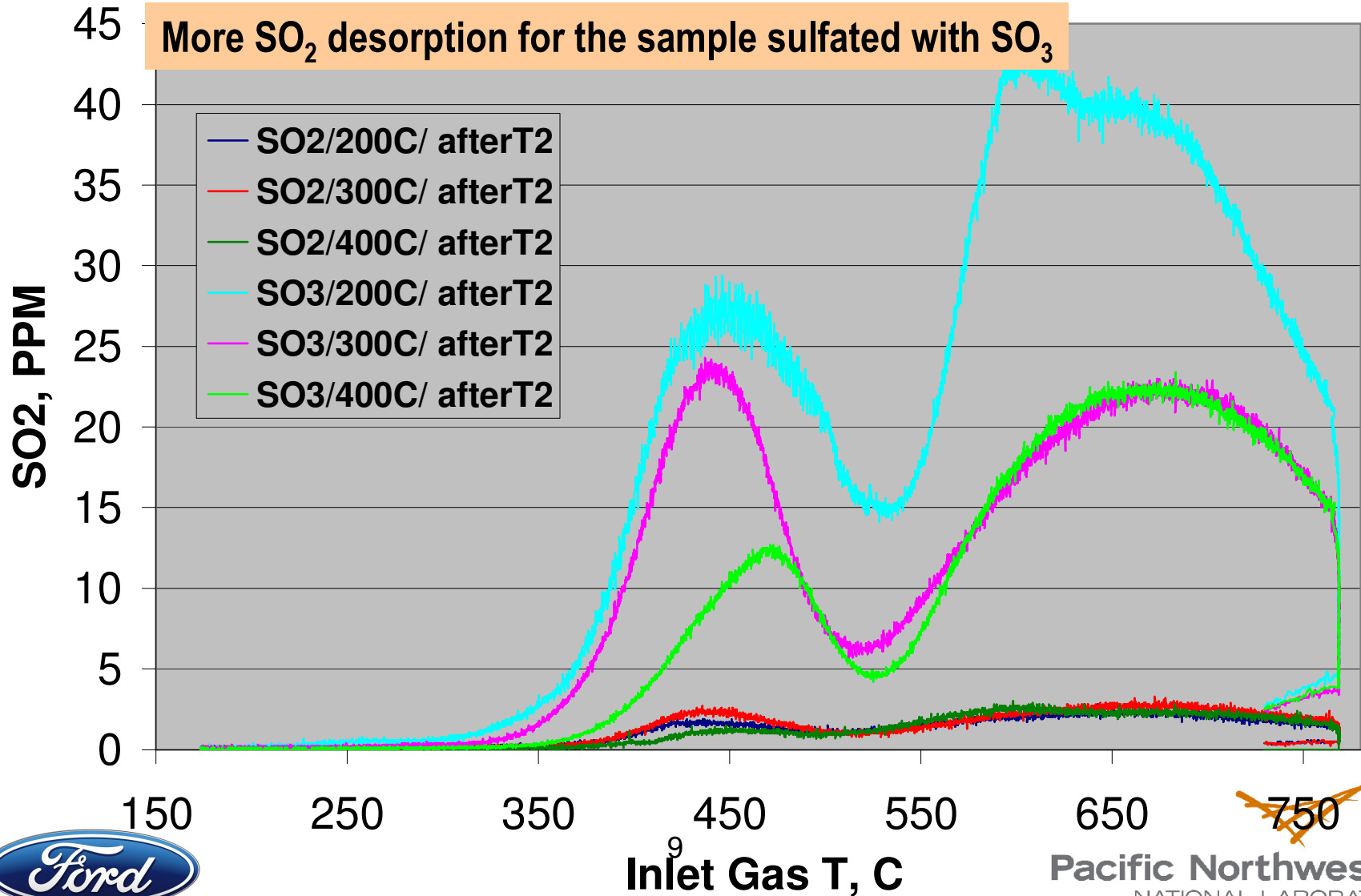


NOx Activity Recovered after DeSOx

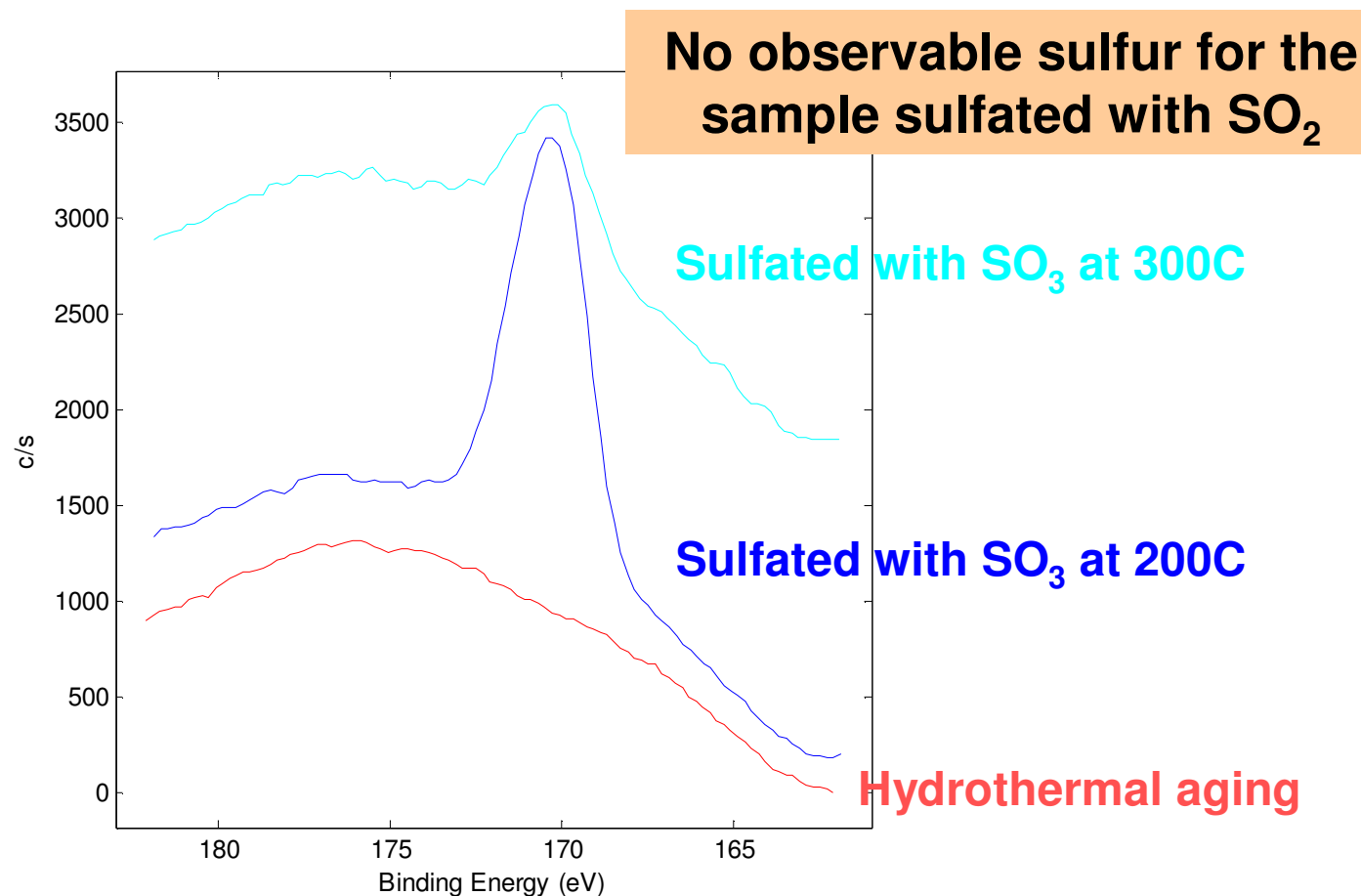


SO₂ vs. SO₃ – Sulfur released during deSO_x

SO₂ Measurement During DeSO_x



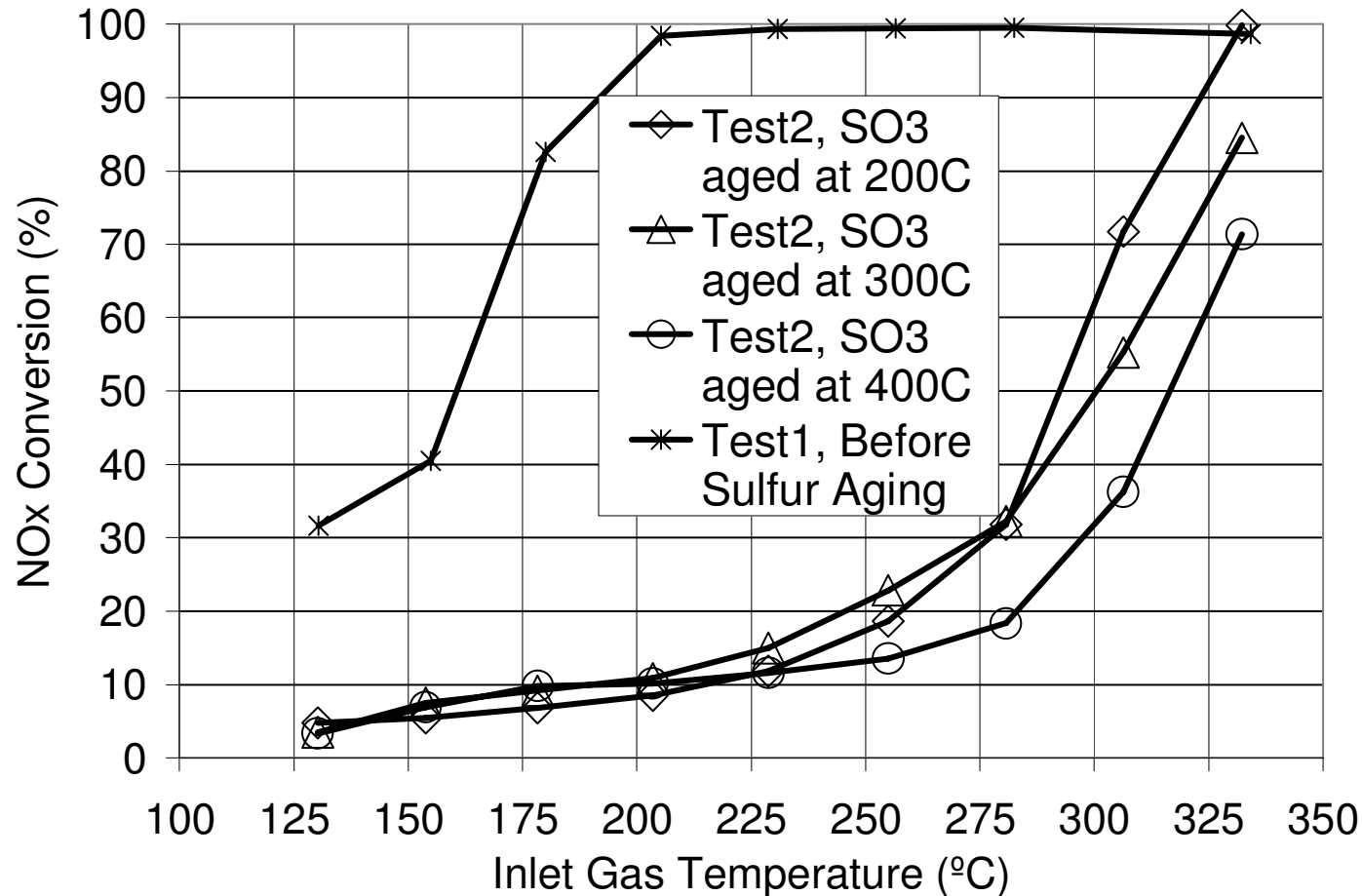
Sulfated with SO_3 : XPS S 2p region



Only sulfates exist, only if sulfated with SO_3 . The sample sulfated with SO_2 does not contain sulfur on the catalyst.

Sulfates formed during reaction at 200C are larger than those at 300C.

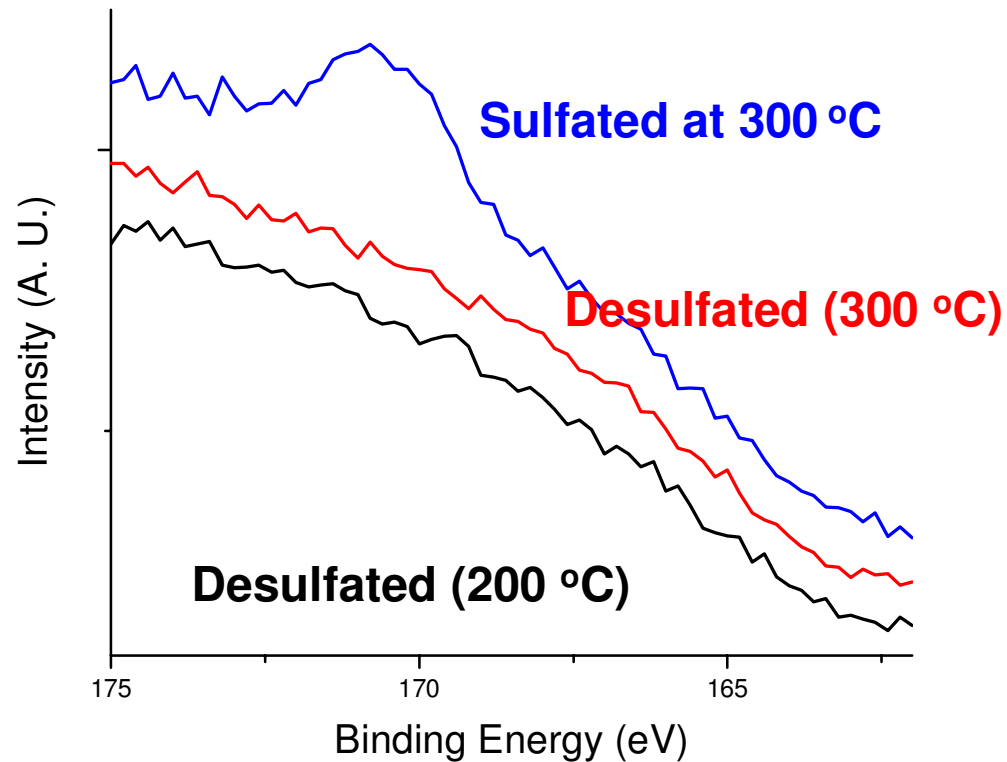
NOx Conversion: sulfated with SO₃ at different T



Not much difference in NOx conversion in spite of higher amount of sulfates over the sample aged at 200C than that at 300C.



After DeSOx: XPS S 2p region



- Sulfur is completely removed after desulfation for both samples.
- Full recovery of NO_x conversion after deSO_x can be explained by the complete removal of sulfate after deSO_x.

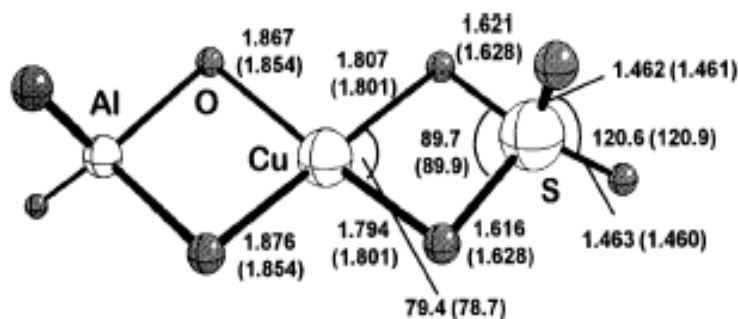


Density functional studies of adsorbates in Cu-exchanged zeolites: model comparisons and SO_x binding

K. C. Hass and W. F. Schneider

Phys. Chem. Chem. Phys., 1999, 1, 639–648

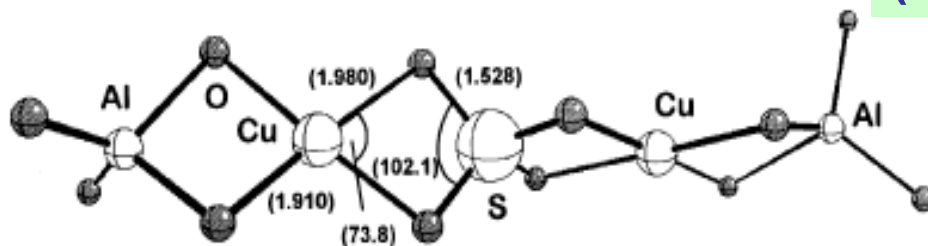
Ford Research Laboratory, MD 3028/SRL, Dearborn, MI 48121-2053, USA



ZCuSO₄ (η^2 -O,O)

ZCuSO₄
Most stable adsorbed SO_x species
better than ZCuSO₃ or ZCuSO₂

Can we identify the species
(structure) with XAFS?



ZCu(SO₄)CuZ

Fig. 7 Same as Fig. 5 for ZCuSO₄ and ZCu(SO₄)CuZ.

XAFS (X-ray absorption fine structure)

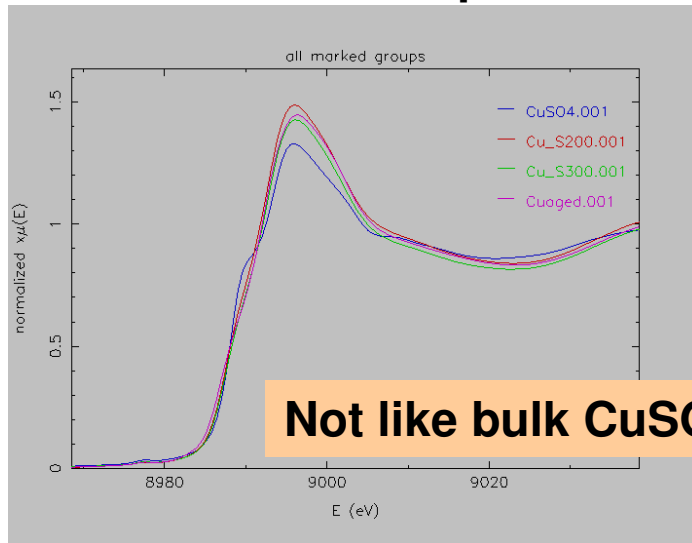
XAFS = XANES (X-ray absorption near-edge spectroscopy) +
EXAFS (extended X-ray absorption fine structure)

- **EXAFS** can give information about bond lengths, element and coordination number surrounding the atom.
- **XANES** yields information about the electronic structure of the absorbing atom, including valence and oxidation state.
- XAFS works for a wide variety of samples: amorphous and crystalline; solid, liquid, and gas; magnetic and nonmagnetic, etc..



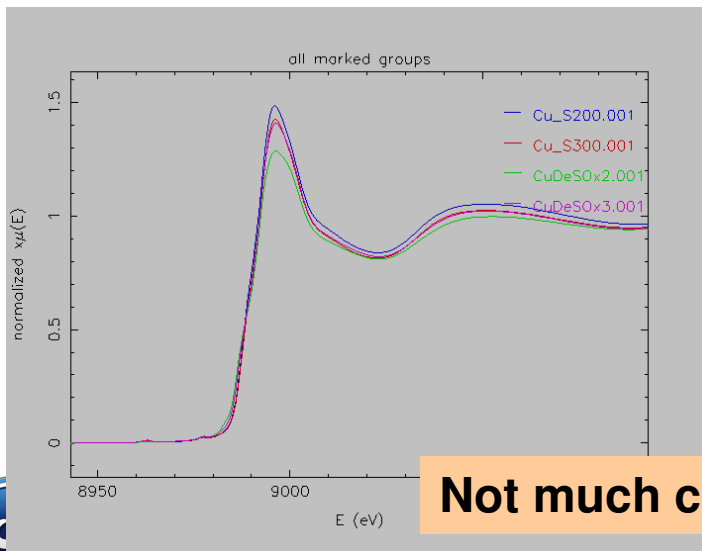
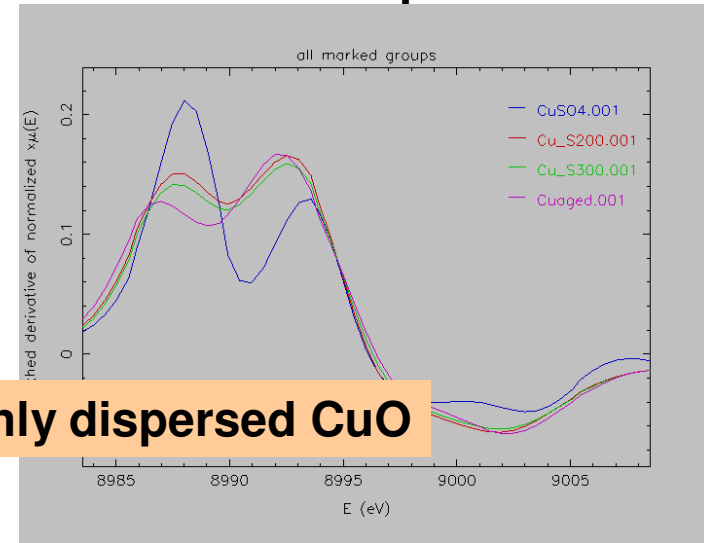
How about the state of Cu?: Cu XANES study

Normalized spectra

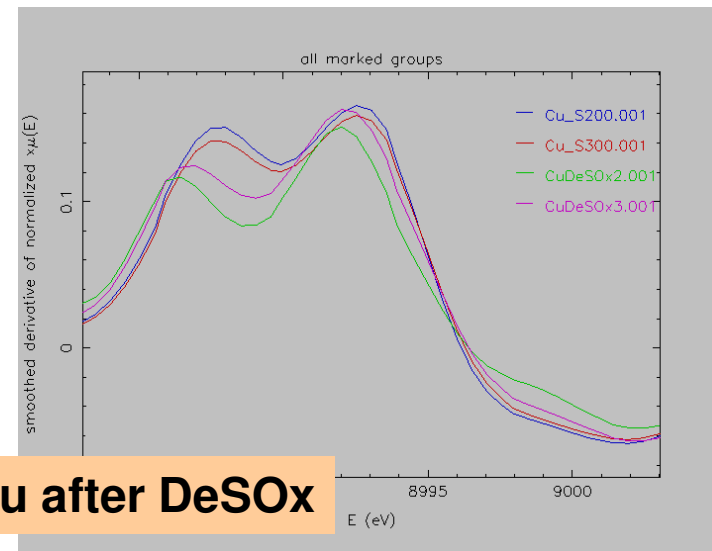


Not like bulk CuSO_4 , but highly dispersed CuO

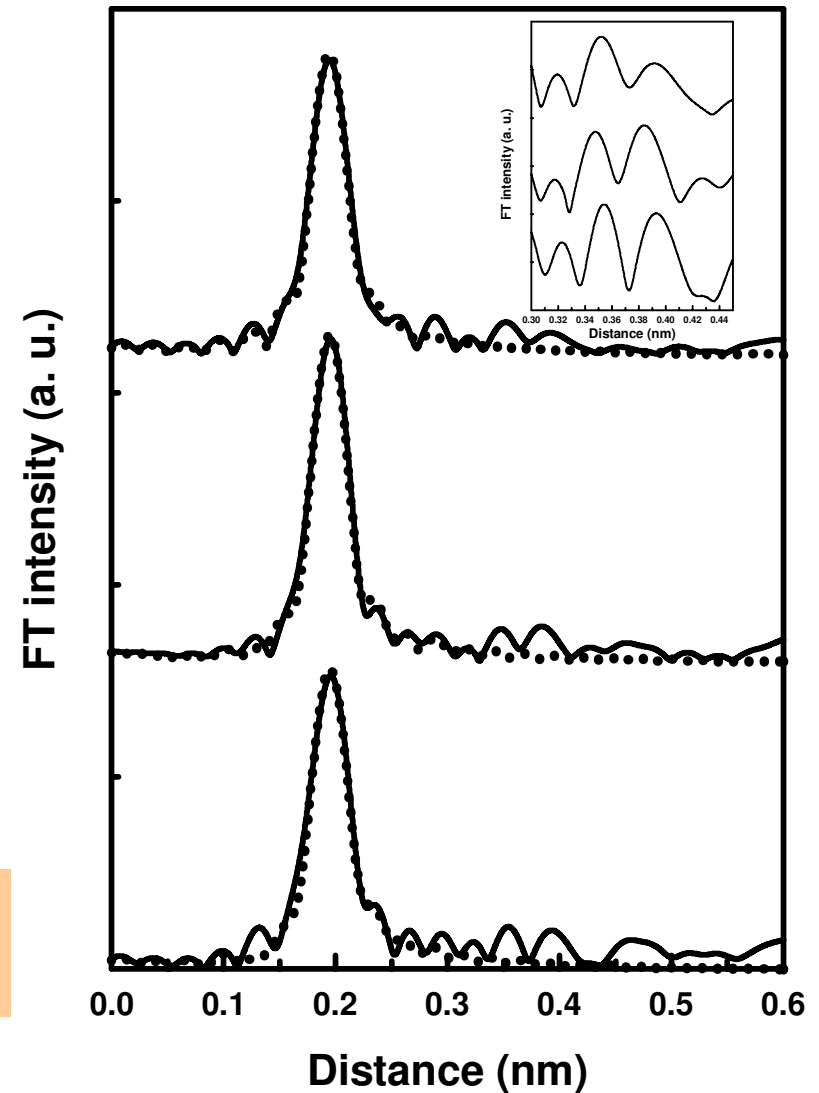
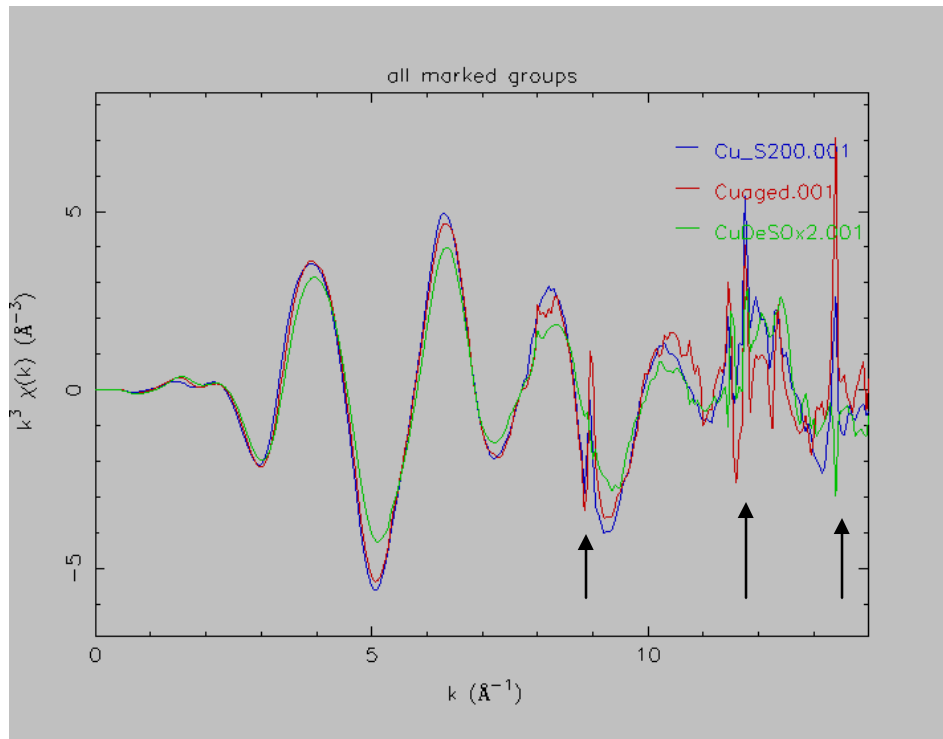
Derivative spectra



Not much change in Cu after DeSOx



Cu XAFS: aged, sulfated with SO₃, DeSOx



Informative, but the 2nd shell structure is not obtained due to the noise signal.



Summary of XAFS curve fitting for Cu sample

Sample	Pair	CN ¹	r (nm) ²	$\sigma^2(\text{pm}^2)$ ³	ΔE (eV)
Cu aged	Cu-O	3.5±0.5	0.195±0.001	57±11	-3.4±2.1
Cu DeSOx	Cu-O	3.4±0.3	0.195±0.001	54±8	-3.4±1.4
Cu sulfated	Cu-O	3.5±0.3	0.195±0.001	46±6	-3.5±1.2

¹Coordination number. ²Coordination distance. ³The Debye-Waller factor accounting thermal and statistical vibration. *The many body reduction factor was fixed to 0.9. The fitting ranges were 20 - 139 nm⁻¹ for Δk and 0.100 – 0.300 nm for Δr , respectively. The restraint was applied to the Debye-Waller factor for the multiple scattering.

Only 1st shell information, which is the same among the samples, is available due to the noisy signal.



Summary

- SCR activity was significantly reduced for samples poisoned by SO_3 compared with those by SO_2 , indicating that sulfur poisoning by SO_2 and SO_3 are not equivalent, with different poisoning mechanisms and impacts.
- Upon the sulfation with SO_3 , Sulfur exists as sulfate forms (not bulk CuSO_4 form, but highly dispersed CuSO_4), but maintain its highly dispersed Cu-O species during SO_x and DeSO_x , which can explain the reversible recovery of activity after desorption as SO_2 at elevated temp.
- This study raises an important sulfur poisoning concern for the systems with DOCs in front of on Cu/zeolite SCR catalysts in diesel engine applications.



Acknowledgement

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