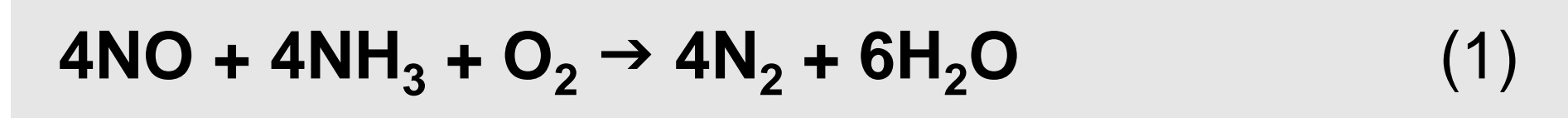


# Identification of the role of metal oxide component of combined metal oxide-SSZ-13 catalyst in improving low-temperature selective catalytic reduction of NOx by ammonia

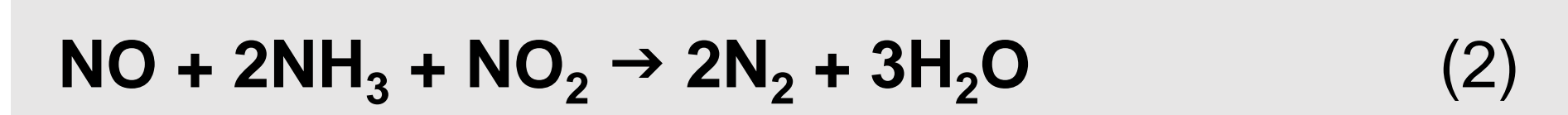
Tahrizi Andana, Kenneth G. Rappe, Feng Gao, Yong Wang  
Pacific Northwest National Laboratory, Richland WA, USA

## BACKGROUND

Selective catalytic reduction (SCR) by ammonia with Cu-SSZ-13 is currently state-of-the-art for controlling NOx emissions from vehicles. NOx is emitted from the engine as predominantly NO, and thus reduction primarily follows the "standard" pathway (eq. 1)



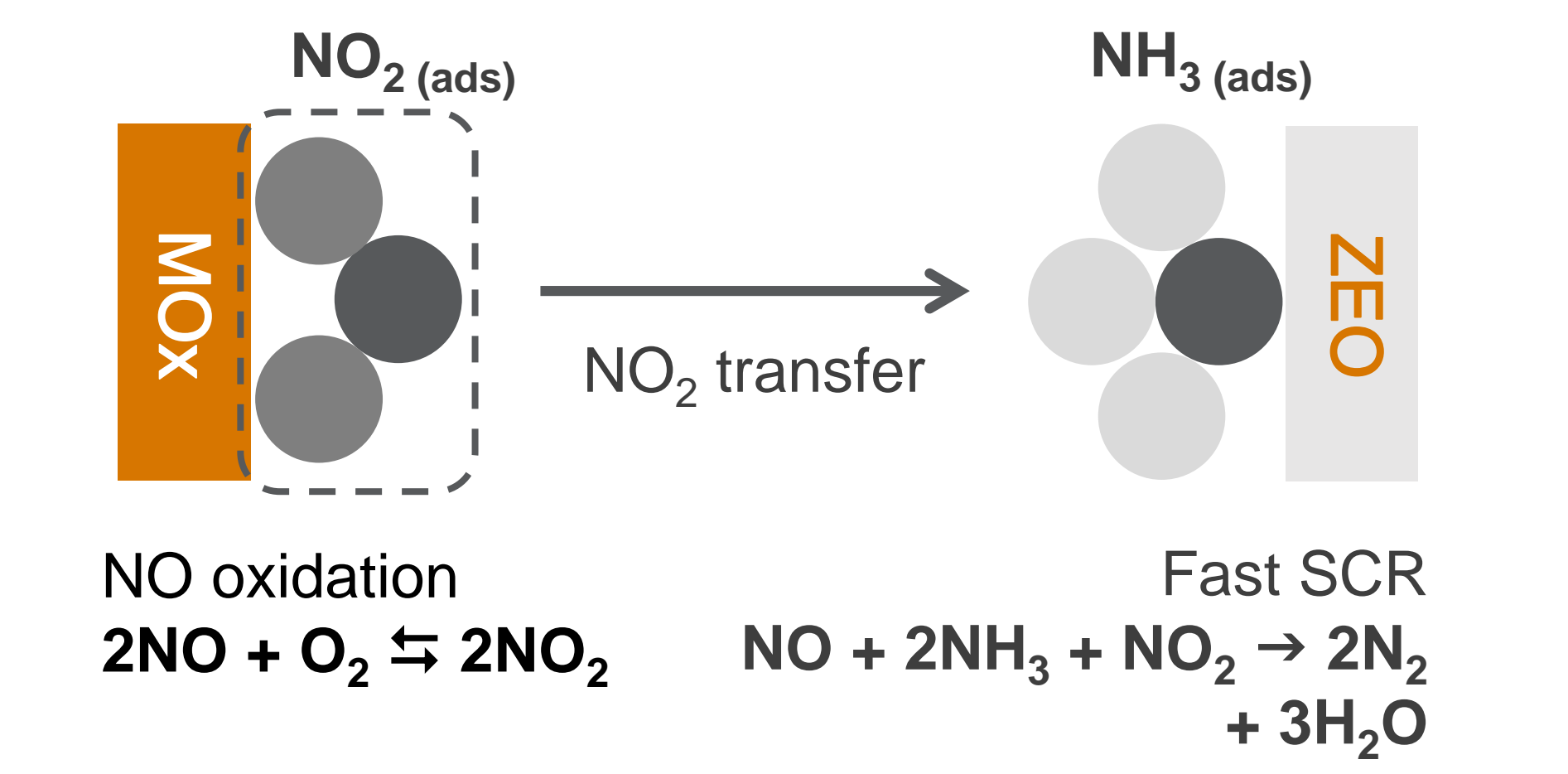
Due to the more stringent emission regulations and combustion advancements, activity improvement becomes necessary by employing a "fast SCR" scheme (eq. 2) at low temperature that uses NO<sub>2</sub> as oxidant



## HYBRID CATALYST

Rare-earth based metal oxide such as cerium oxide ("ceria", CeO<sub>2</sub>) can catalyze NO oxidation to NO<sub>2</sub>.

Coupling metal oxide and zeolite component helps selectively generate NO<sub>2</sub> in situ for faster SCR via bifunctional mechanism<sup>1,2</sup>



## OBJECTIVE

The present study aims at identifying the role and extent of participation of the metal oxide component in promoting synergistic effects on the low-temperature SCR reaction

- References**
- Salazar et al., Appl Catal B. 165 (2015) 316-327
  - Stakheev et al., Catal Today 258 (2015) 183-189
  - Qi and Yang, J Catal 217 (2003) 434-411
  - Gao et al., J Catal 331 (2015) 25-38

contact info: ken.rappe@pnnl.gov (509) 372-4413

## SAMPLES

### ZEOLITE COMPONENT

- H-SSZ-13 (HSZ)**, prepared in-house via hydrothermal synthesis (Si/Al = 12, S<sub>BET</sub> = 800 m<sup>2</sup> g<sup>-1</sup>)
- Cu-SSZ-13 (CSZ)**, prepared via ion-exchange (Cu/Al = 0.2, Cu = 1.4 wt%)

### OXIDE COMPONENT

**Ceria-manganese oxide (CM)** (Ce-to-Mn ratio = 7:3) prepared via thermal decomposition of nitrate salt precursors (S<sub>BET</sub> = 35 m<sup>2</sup> g<sup>-1</sup>)

### COMBINED CATALYST

- Variation of oxide loading**, prepared with 1 – 25 wt% oxide-to-zeolite ratio and impregnation as coupling technique
- Variation of degree of separation**, prepared with 10 & 25 wt% oxide-to-zeolite ratio and various coupling techniques: impregnation (IM), ball-milling (BM) and loose mixing (LM)

## TESTING

Catalytic activity testing was carried out via temperature-programmed reaction using 400 L g<sup>-1</sup> h<sup>-1</sup> mass space velocity and 2 °C min<sup>-1</sup> heating rate

**Standard SCR test** was conducted with 350 ppm NO, 350 ppm NH<sub>3</sub>, 15 vol% O<sub>2</sub>, 8 vol% CO<sub>2</sub> and 6 vol% H<sub>2</sub>O (balanced N<sub>2</sub>)

## KINETICS

SCR reaction rate was modelled via power law, first order of NO<sup>3,4</sup>

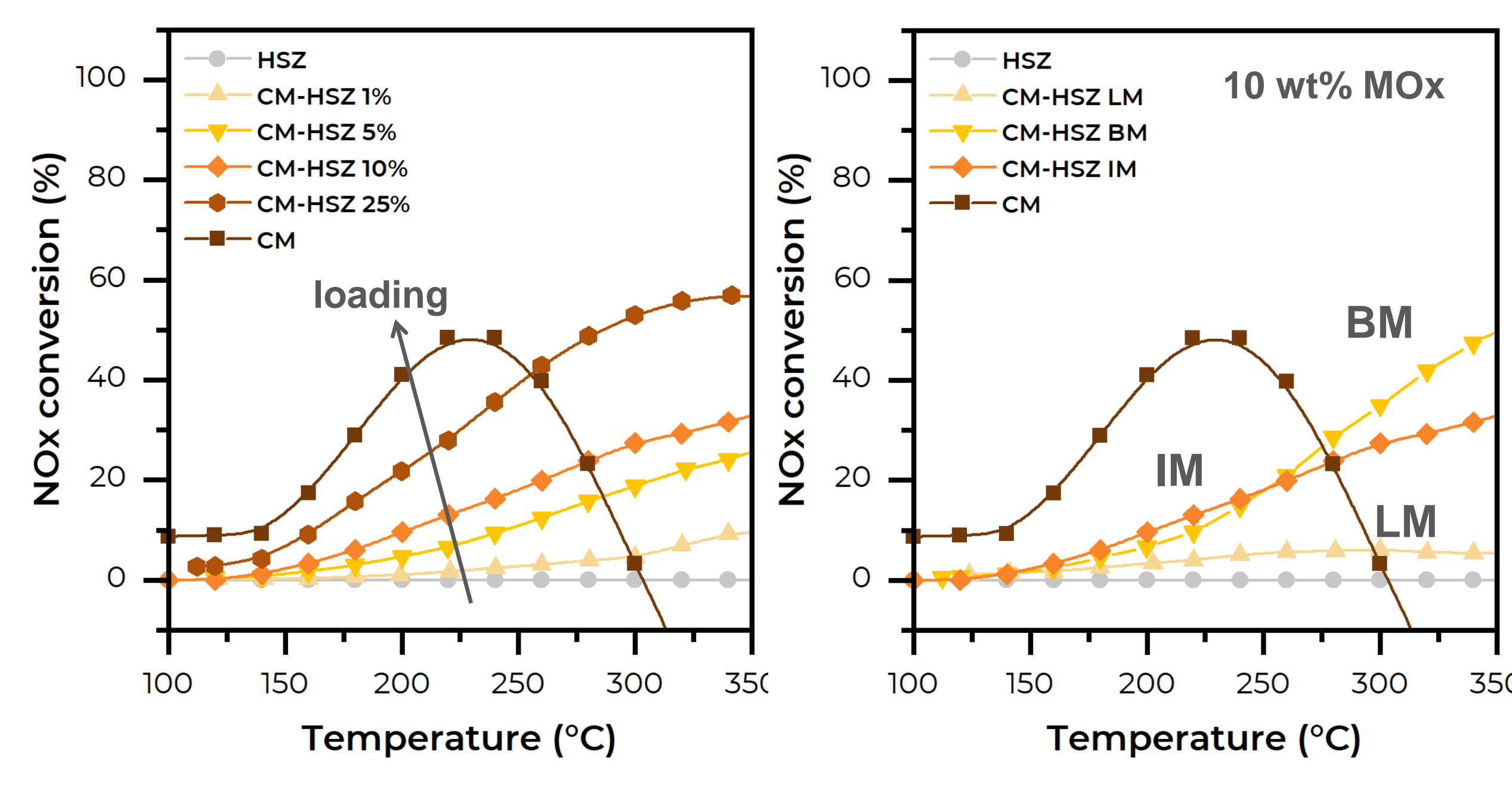
$$r = k [\text{NO}]_0 (1-x)$$

Kinetics parametrization through combining Arrhenius equation and plug flow reactor balance

$$\ln(-\ln(1-x)) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln Ar$$

[NO]<sub>0</sub> = feed NO conversion, x = NO conversion, E<sub>a</sub> = activation energy (kJ mol<sup>-1</sup>), τ = residence time (cm<sup>-3</sup> g s)

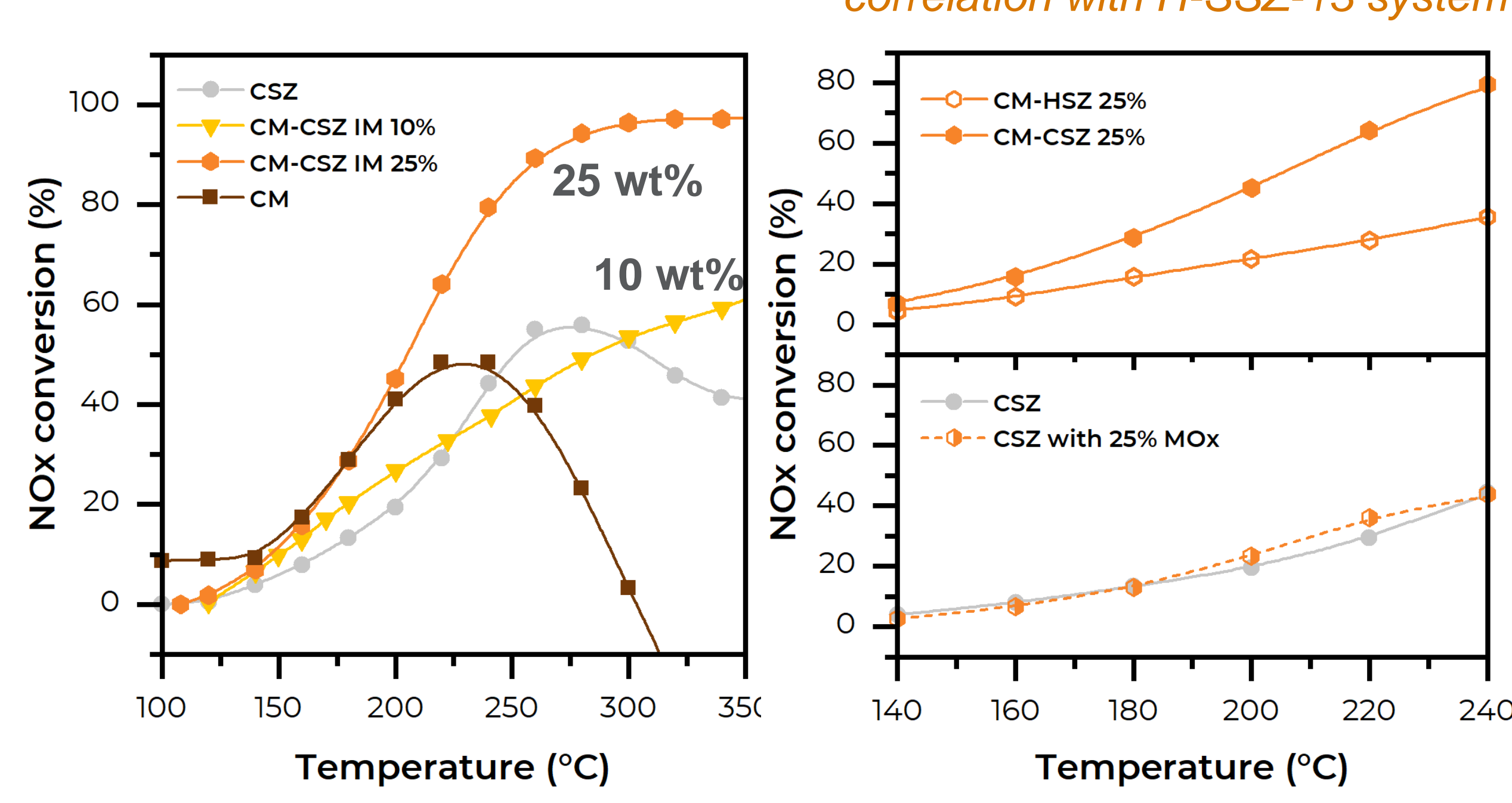
## COMBINED MOx/H-SSZ-13



[LEFT] As the metal oxide loading increases, light-off conversion increases. Synergistic effect on the low-temperature reaction is directly proportional to the amount of deposited metal oxide

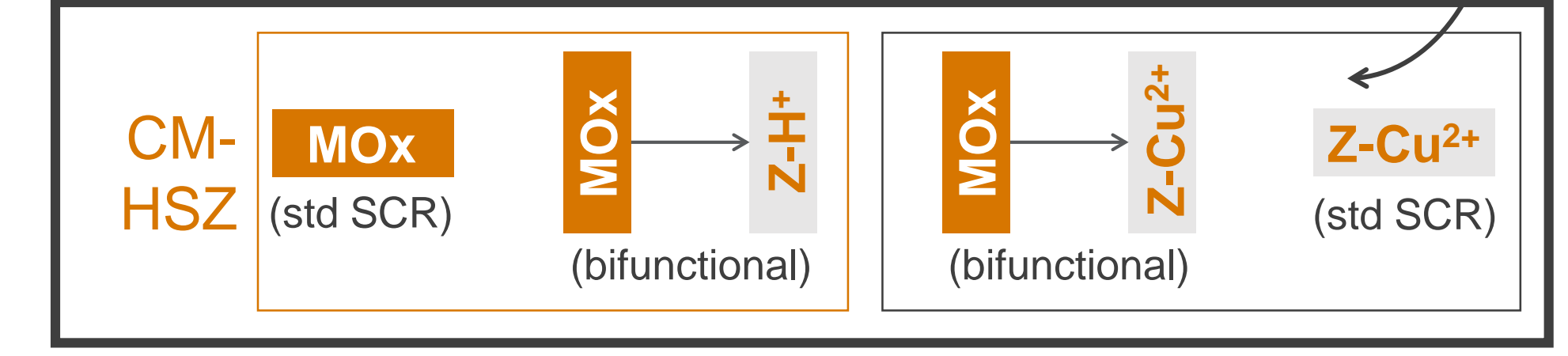
[RIGHT] Degree of contact between the oxide and zeolite components also determines the synergistic effect

## COMBINED MOx/Cu-SSZ-13

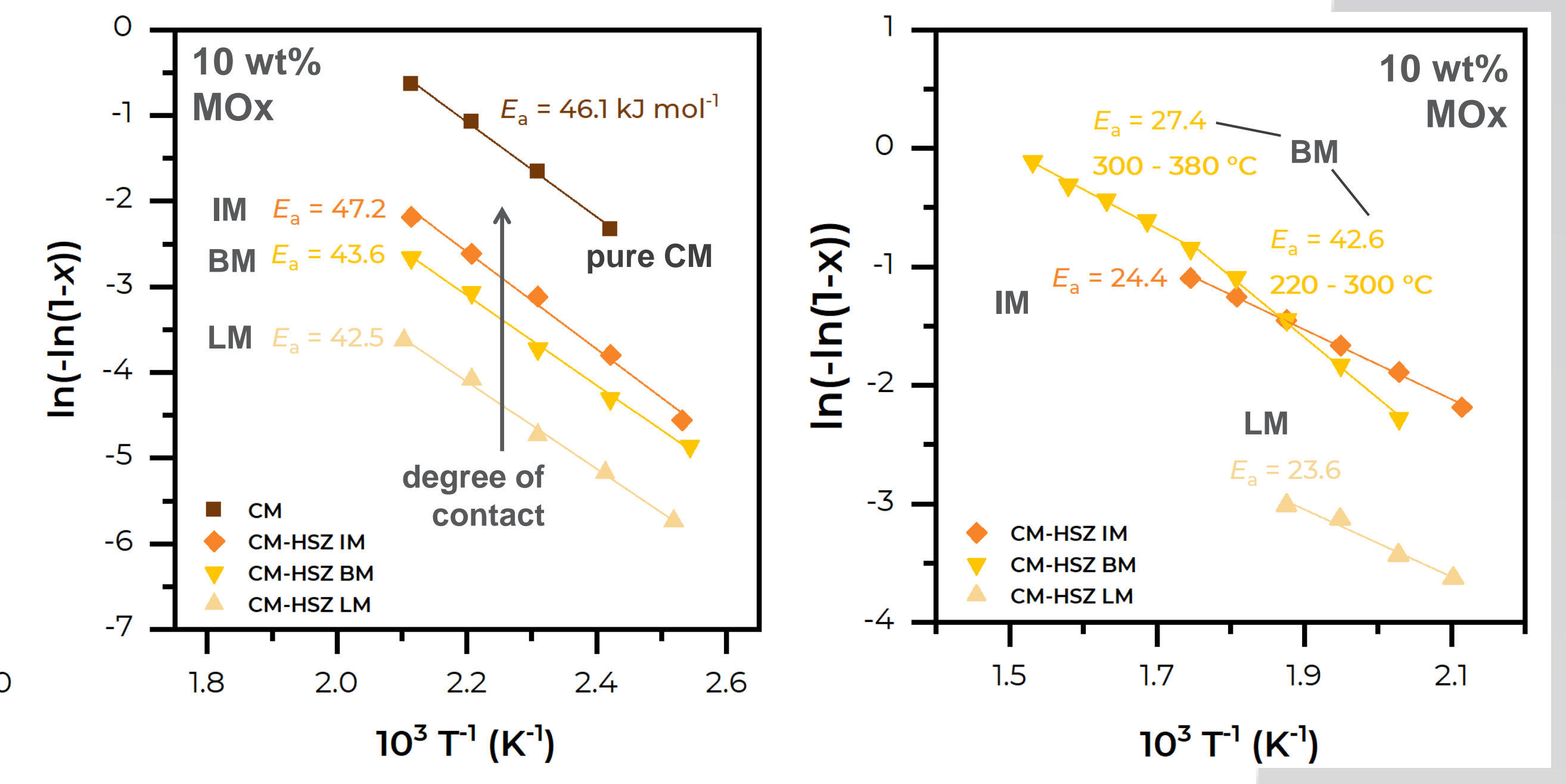


[LEFT] The presence of metal oxide up to 25 wt% induces an improved light-off conversion. It also alters the SCR mechanism over Cu-SSZ-13 (disappearance of "seagull" shape)

[RIGHT] Subtracting the performance data of CM-HSZ from that of CM-CSZ (top) yields the performance data of Cu-related reactions in the presence of MOx (bottom)



## MOx/H-SSZ-13 KINETICS



**120–200 °C**  
Kinetically controlled regime  
E<sub>a</sub> CM-HSZ ≈ E<sub>a</sub> CM (42 – 47 kJ mol<sup>-1</sup>)

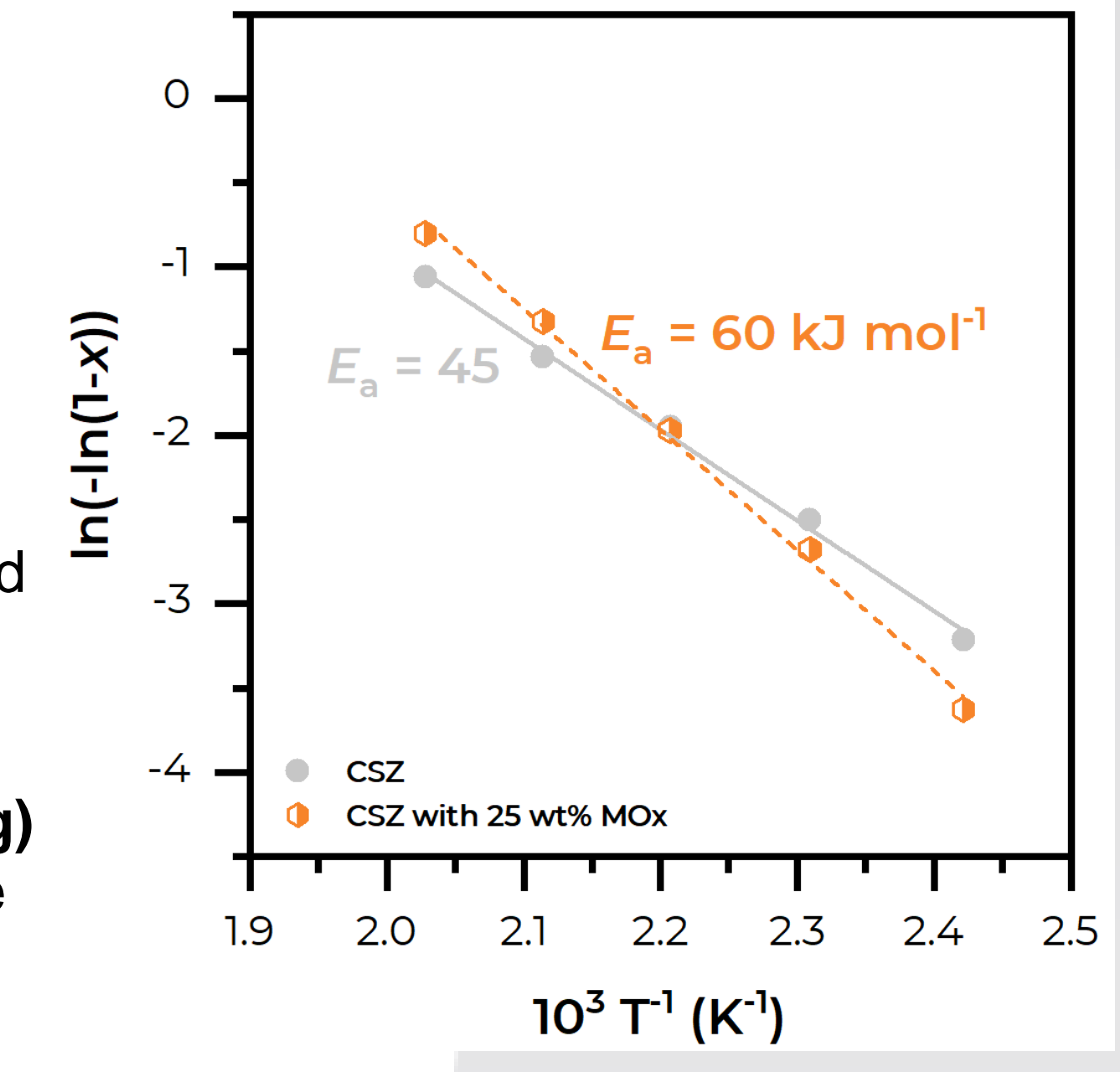
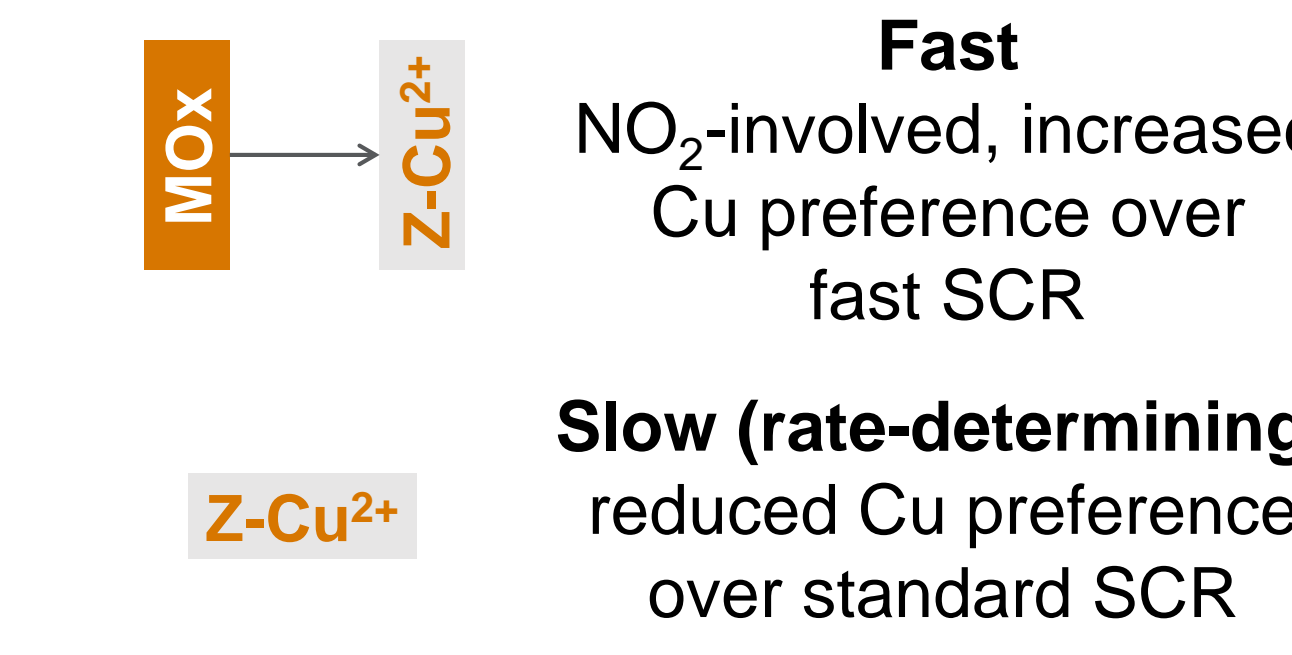
- E<sub>a</sub> similarity indicates direct participation of the oxide component
- Variation of reaction rate reflects mutual participation of the two components

**240–300 °C**  
Diffusion-controlled regime  
E<sub>a</sub> CM-HSZ ≈ 1/2 E<sub>a</sub> CM (23 – 27 kJ mol<sup>-1</sup>)

- Reaction rate increases so greatly with temperature it surpasses diffusion rate
  - Extended kinetic regime observed for ball-milled catalyst indicates higher diffusion rate due to the decrease of particle size
- SEM images demonstrate larger and more clumping oxide particles in the impregnated sample than in the ball-milled counterpart

## MOx/Cu-SSZ-13 KINETICS

Higher E<sub>a</sub> observed for Cu-related reactions in the presence of MOx highlights an interplay of these two reactions:



## CONCLUSION

- Participation of metal oxide in low-temperature SCR reaction can be direct (on MOx surface) and/or indirect (via both MOx and zeolite phases)
- Bifunctional mechanism occurs so fast it can render the reaction over the zeolite diffusion-controlled; morphology control and exchanged metal species can alleviate this issue