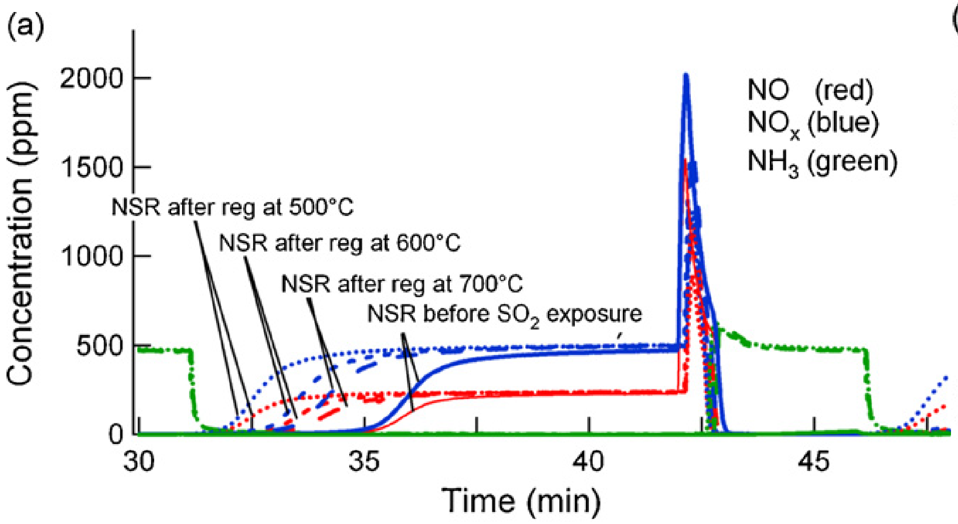
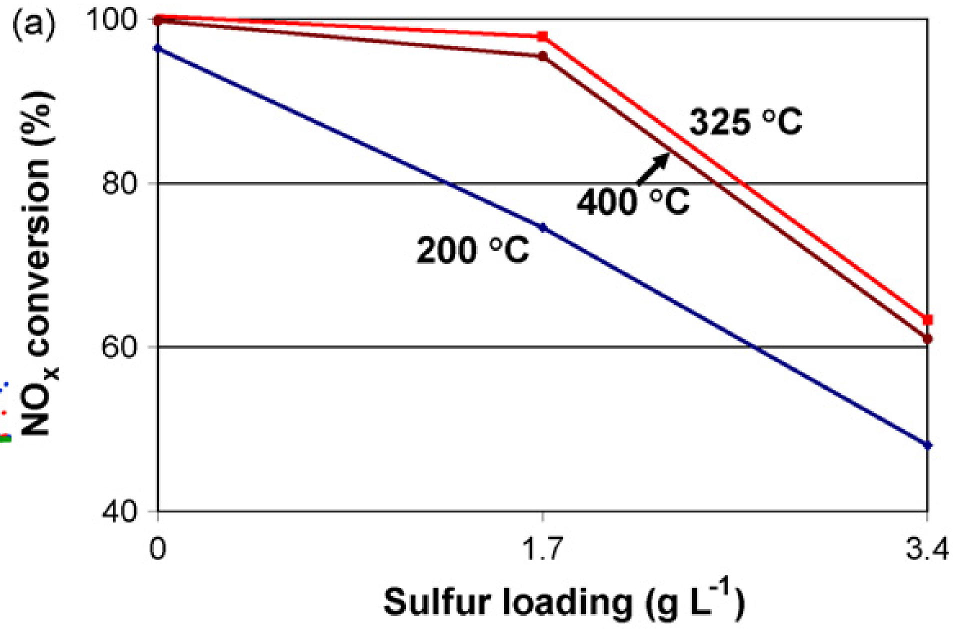
SO_2 Oxidation over a Pt/Al_2O_3 Catalyst

Tayebeh Hamzehlouyan, Chaitanya Sampara,
Junhui Li, Ashok Kumar and Bill Epling

Background (S impact on LNT)

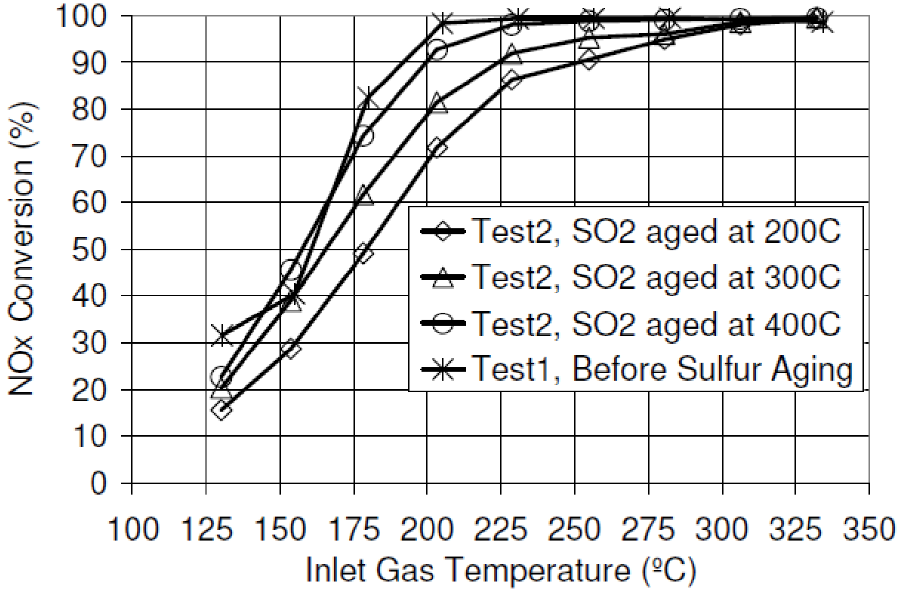


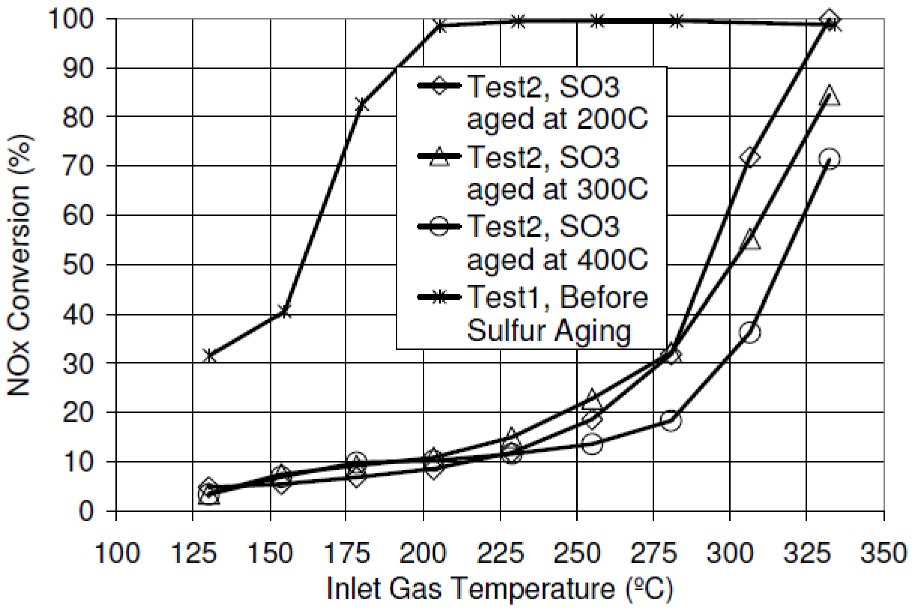


Known and significant impact on LNT catalysts

L. Olsson, M. Fredriksson, R.J. Blint, Appl. Catal. B 100(2011)31.
J.-S. Choi, W.P. Partridge, J.A. Pihl, C.S. Daw, Catalysis Today 136(2008)173.

Background (S impact on SCR)

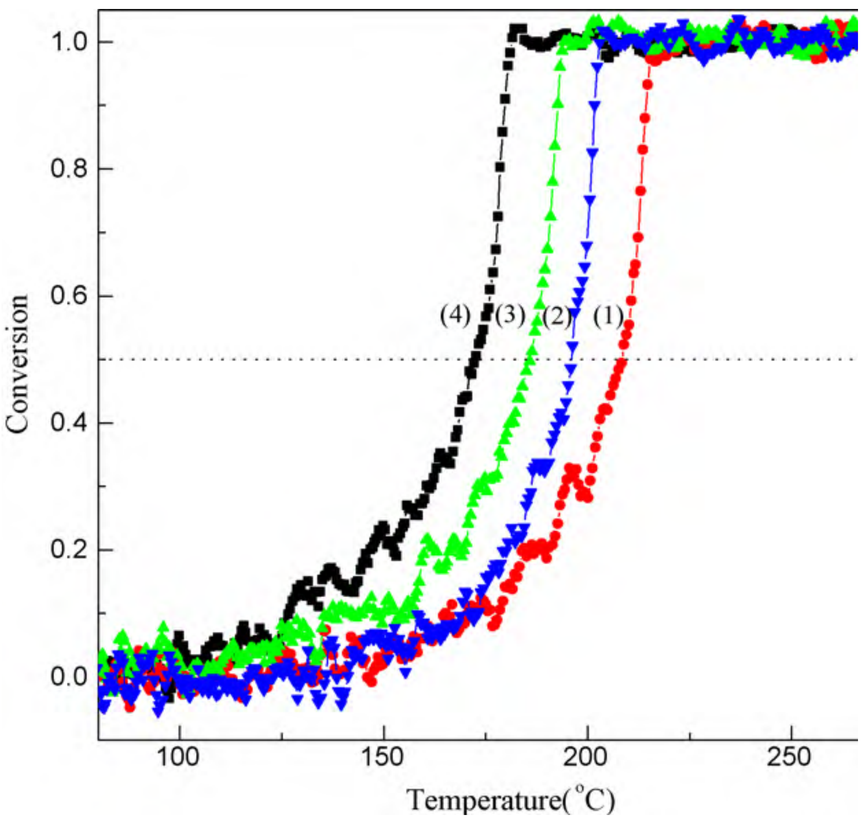


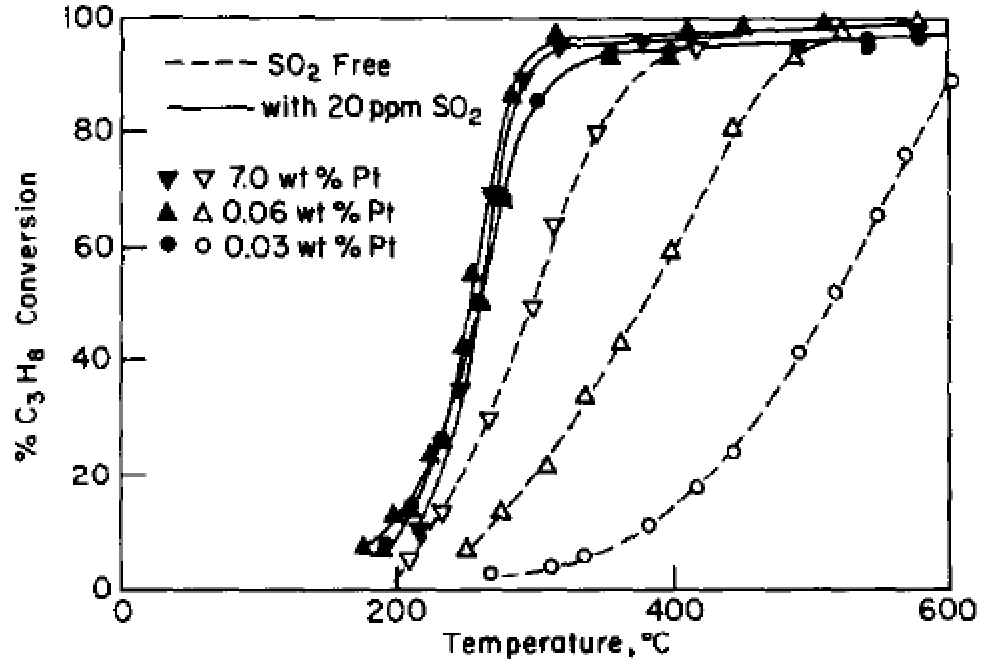


Known and significant impact on SCR catalysts

Y. Cheng, C. Montreuil, G. Cavataio and C. Lambert, SAE Technical Paper Series 2009-01-0898.

Background (S impact on oxidation catalysis)





Known and significant impact on DOCs

J.-Y. Luo, D. Kisinger, A. Abedi, W.S. Epling, Appl. Catal. A 383(2010)182.
H.C. Yao, H.K. Stepien and H.S. Gandhi, Journ. Catal.67(1981)231.

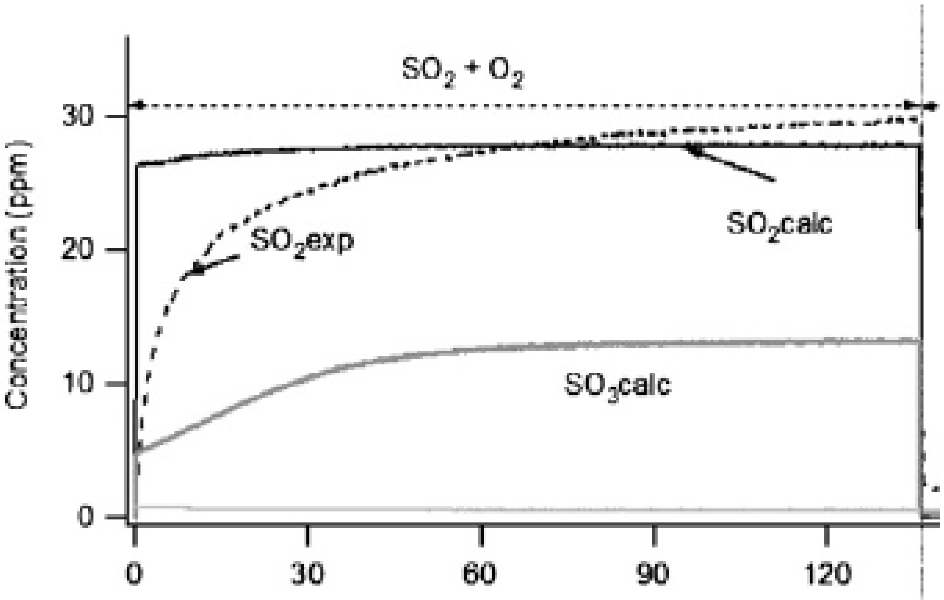
SO_2 oxidation

- SO_2 oxidation over Pt-based catalysts
  - SO_2/SO_3 adsorption have highest sensitivity coefficients
  - Most studies based on large SO_2 concentrations
  - Dawody, S poisoning of LNTs

$$SO_2(g) + Pt \underset{32}{\overset{31}{\longleftrightarrow}} Pt{-}SO_2$$

$$Pt{-}O + Pt{-}SO_2 \underset{34}{\overset{33}{\longleftrightarrow}} Pt{-}SO_3 + Pt$$

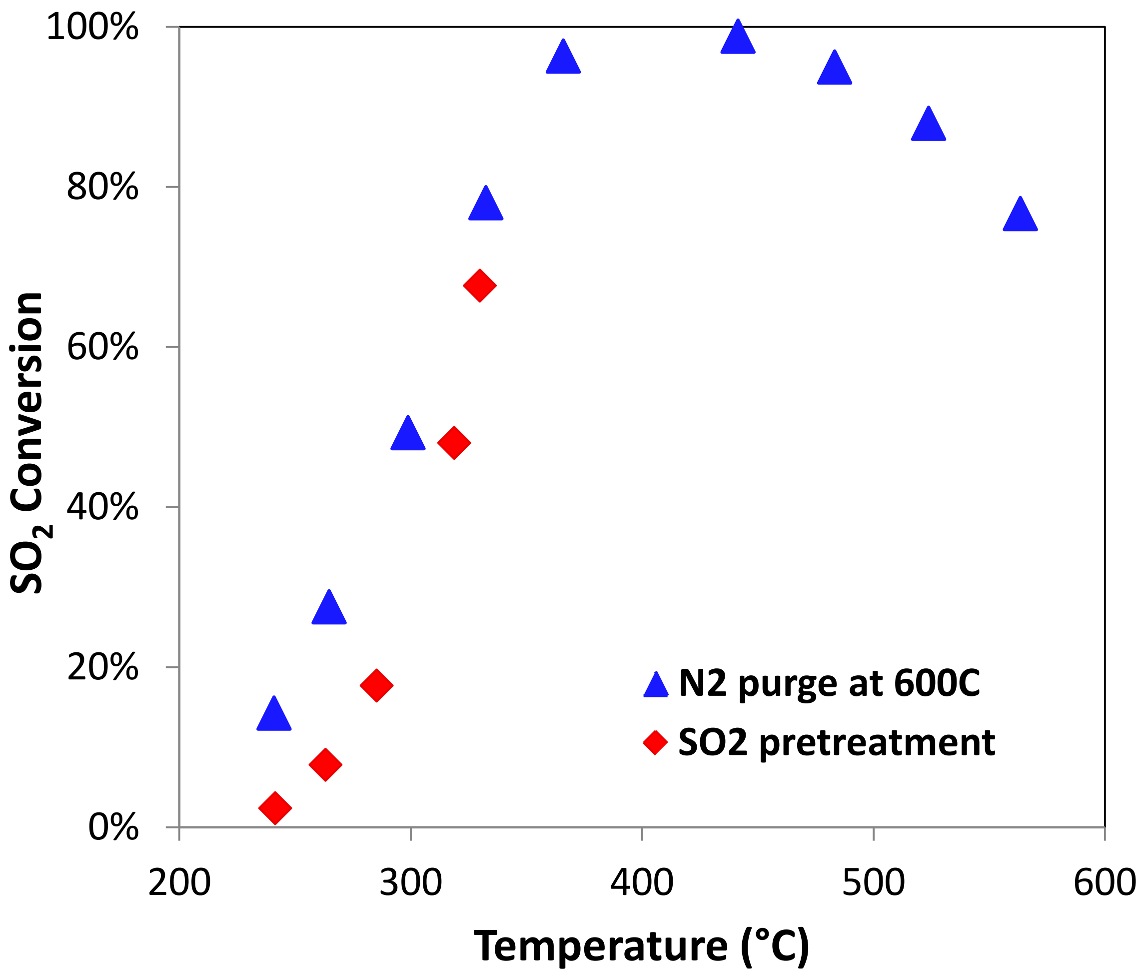
$$Pt{-}SO_3 \underset{36}{\overset{35}{\longleftrightarrow}} Pt + SO_3(g)$$



Experimental Methodology

- Pt/Al_2O_3 catalyst
  - 50 g/ft^3 Pt, 6% dispersion (CO chemisorption)
- MKS 2030 FTIR for gas-phase analysis
  - SO_2 and SO_3 calibrations built in-house
  - Instrument modified with $ZnSe/MgF_2$ windows
  - Restek coated lines
- Steady-state conditions established for data to be shown

Effect of pretreatment



$$SO_2 + \frac{1}{2}O_2 \leftrightarrow SO_3$$

Pretreatment methods:

N_2 purge

N_2 at T≈600°C for 1 hour

SO_2 pretreatment

50 ppm SO_2 at T≈240°C overnight

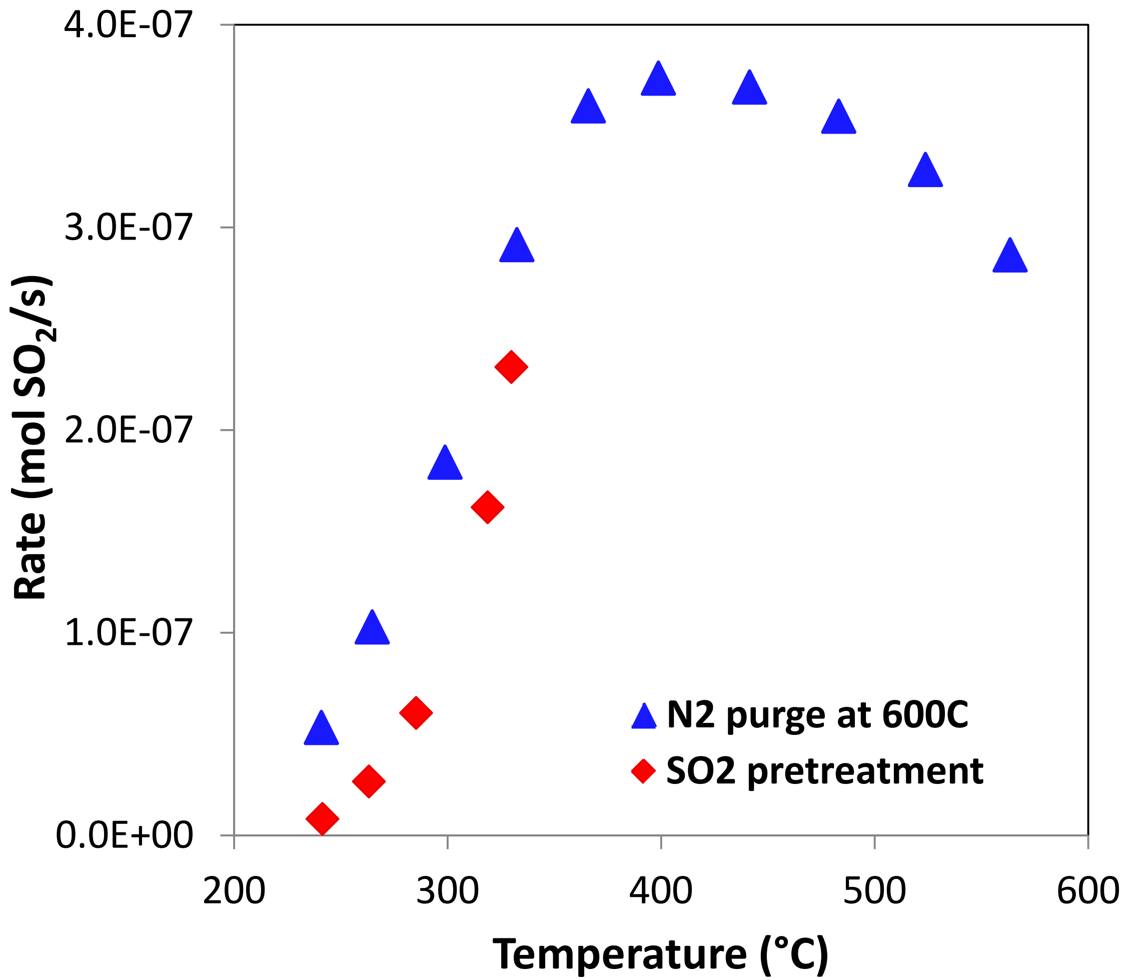
Feed:

$[SO_2]$ = 100 ppm

$[SO_3]$ = 75 ppm

$[O_2]$ = 10%

Effect of pretreatment



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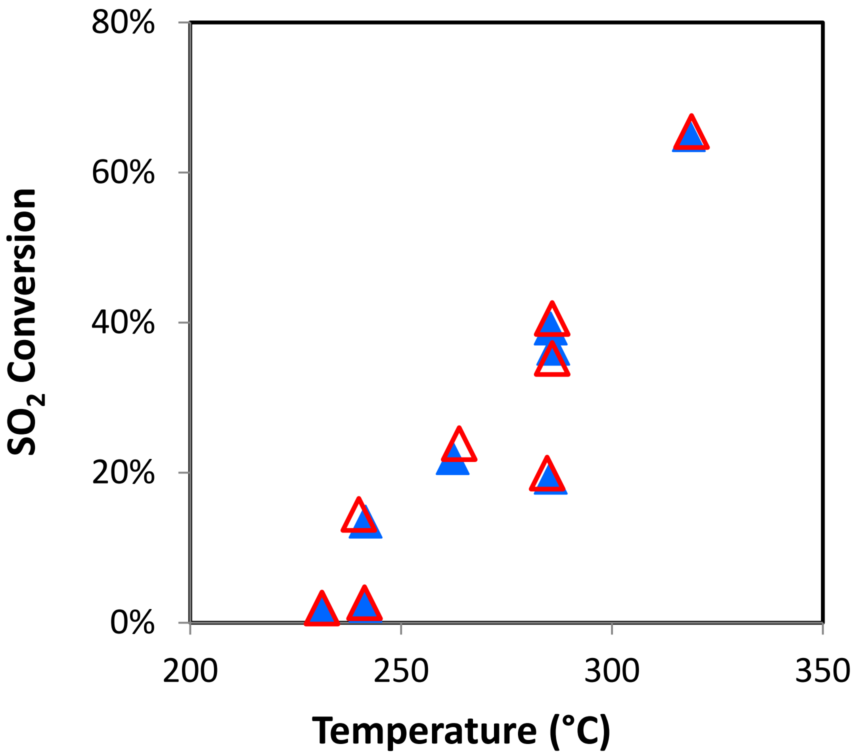
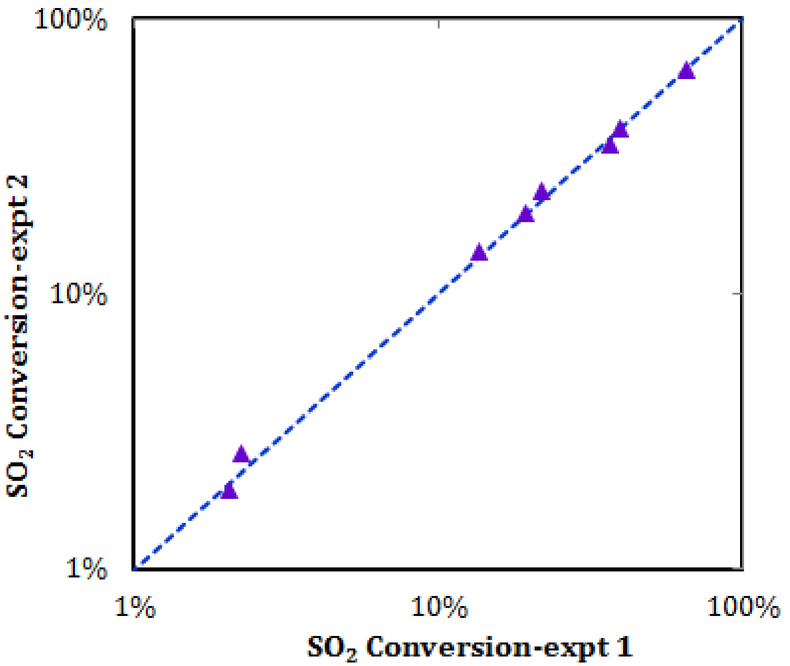
Data reproducibility

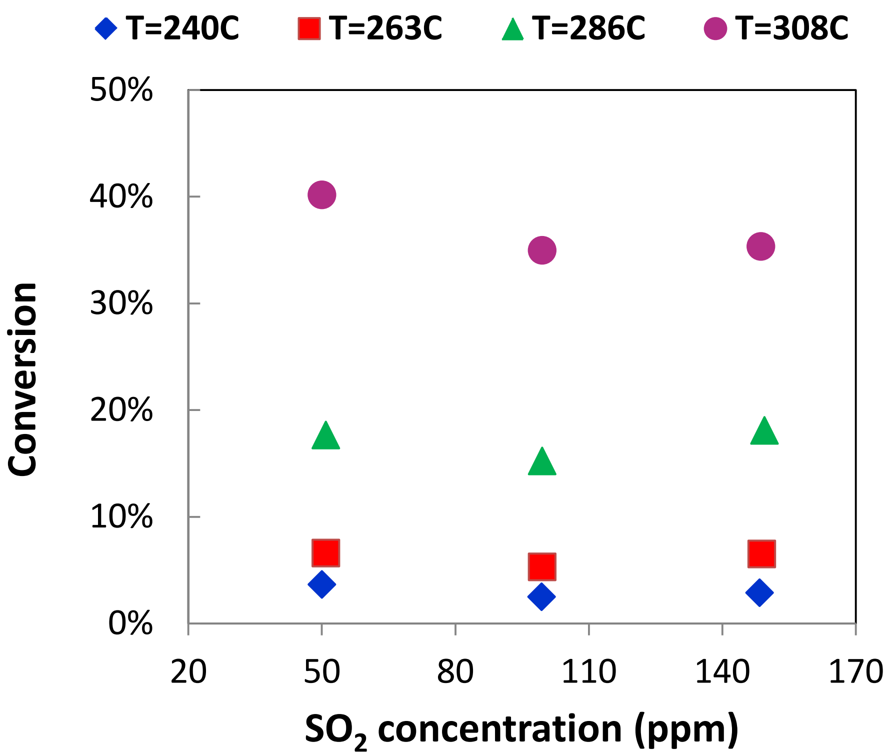


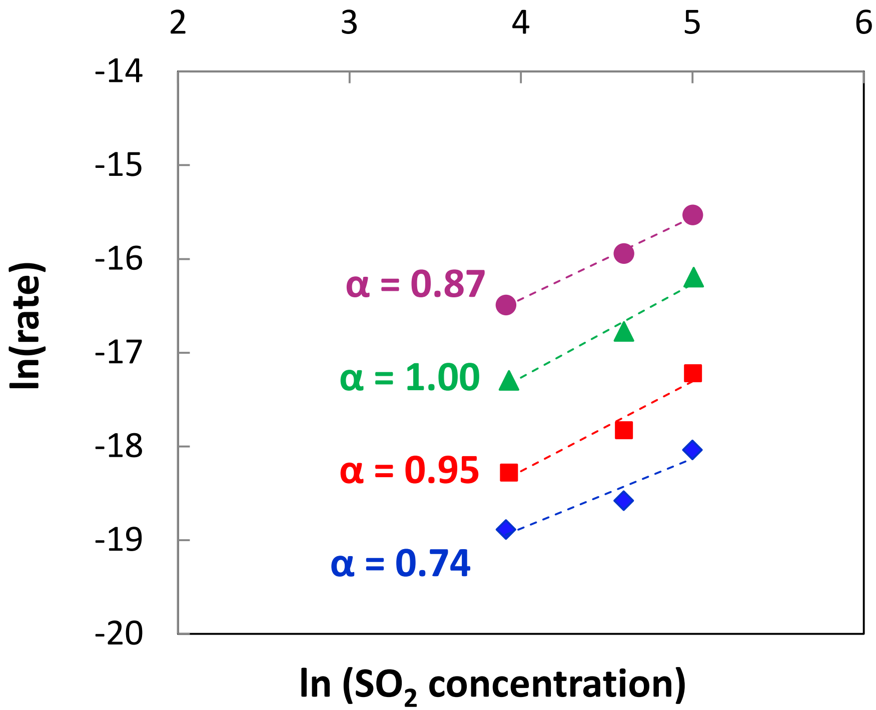


T (°C)	SO_2(ppm)	SO_3(ppm)	O_2(%)
231.4	100	50	10
241.5	150	100	10
241.5	50	0	10
285.4	100	0	5
285.4	50	100	7
262.2	100	0	5
318.2	100	0	10
286.0	100	0	10

"Long" pretreatment critical in obtaining good reproducibility

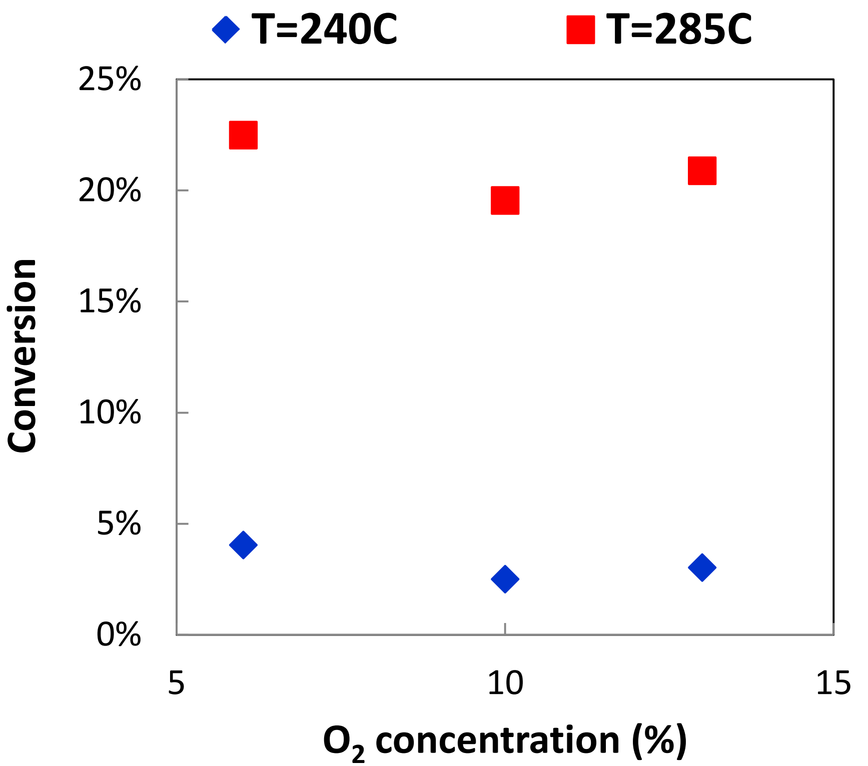
Effect of SO_2 on performance

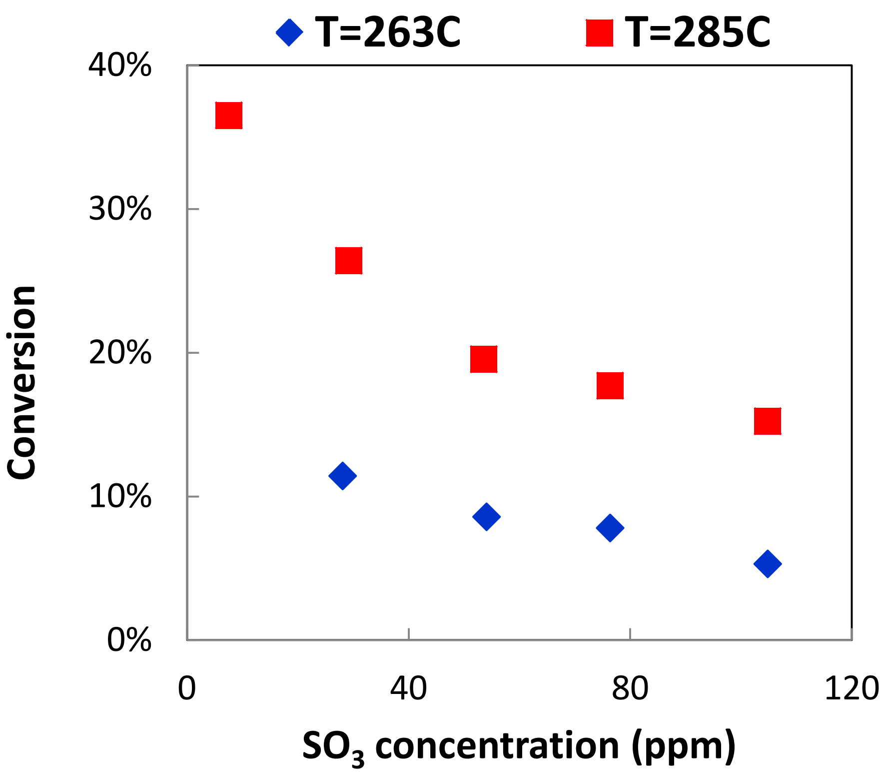




Change in SO_2 concentration leads to similar conversions → first order dependence

Effect of O_2 and SO_3





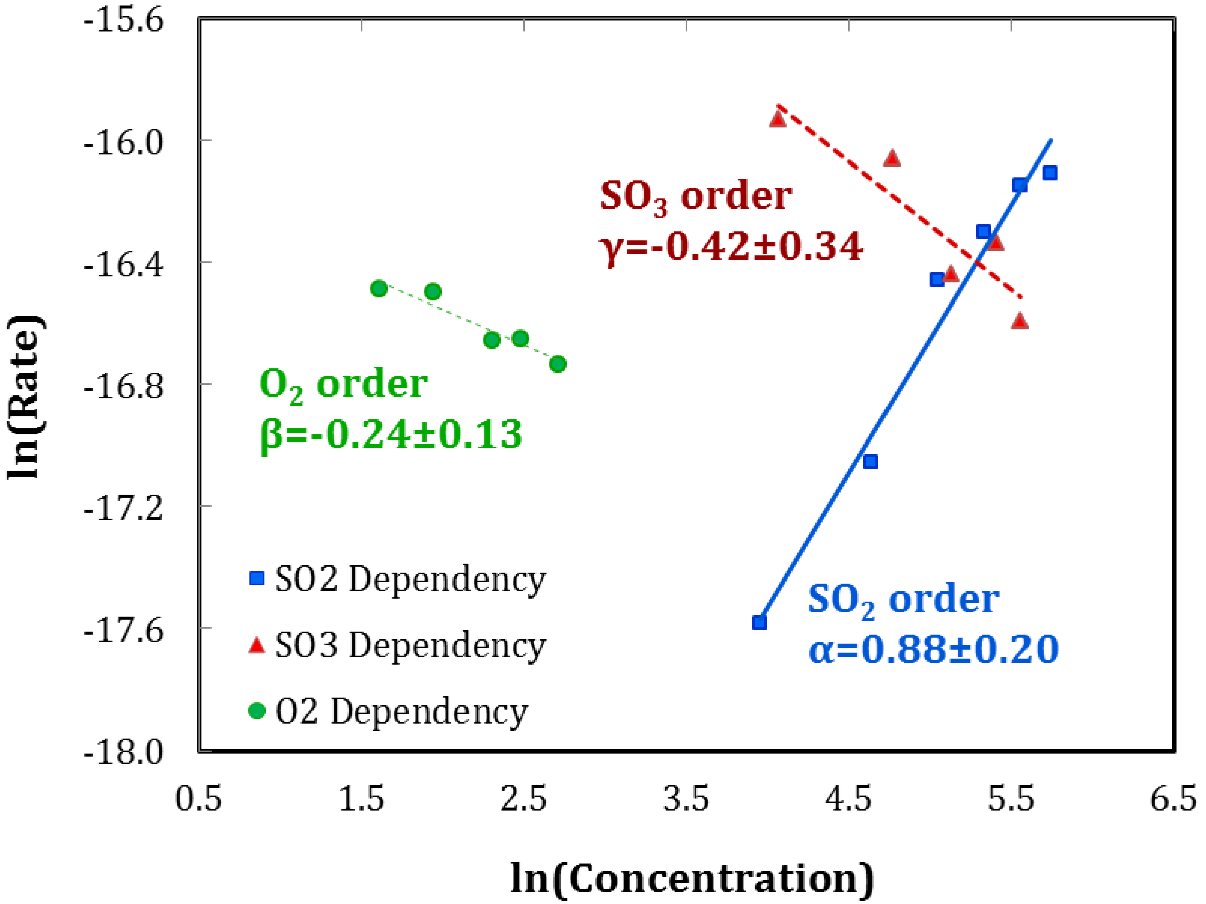
O_2 seems to have a slight negative effect on SO_2 oxidation

SO_3 has a definite negative impact (product inhibition)

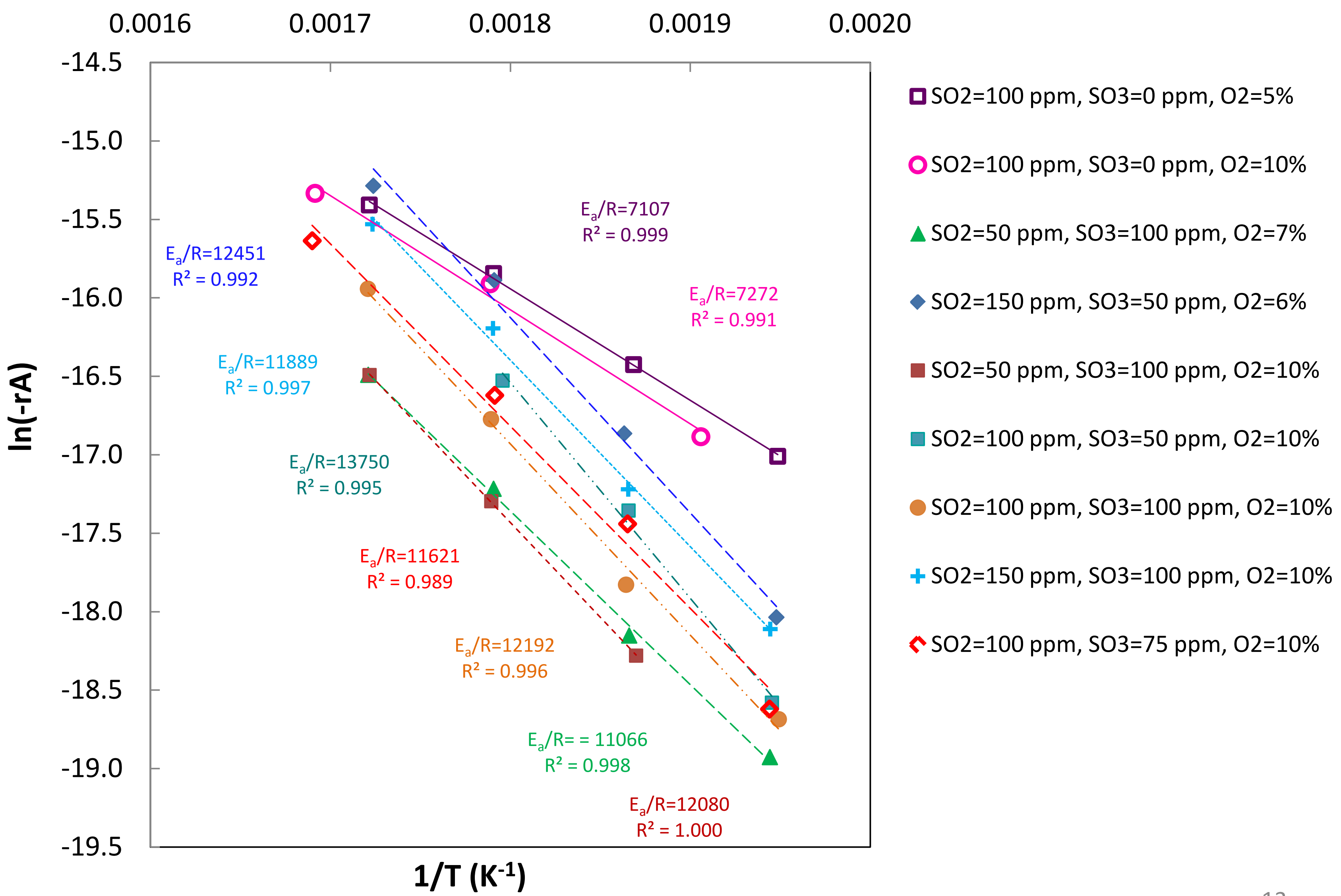
Reaction rate dependencies summary

SO_2 oxidation over Pt/Al_2O_3:

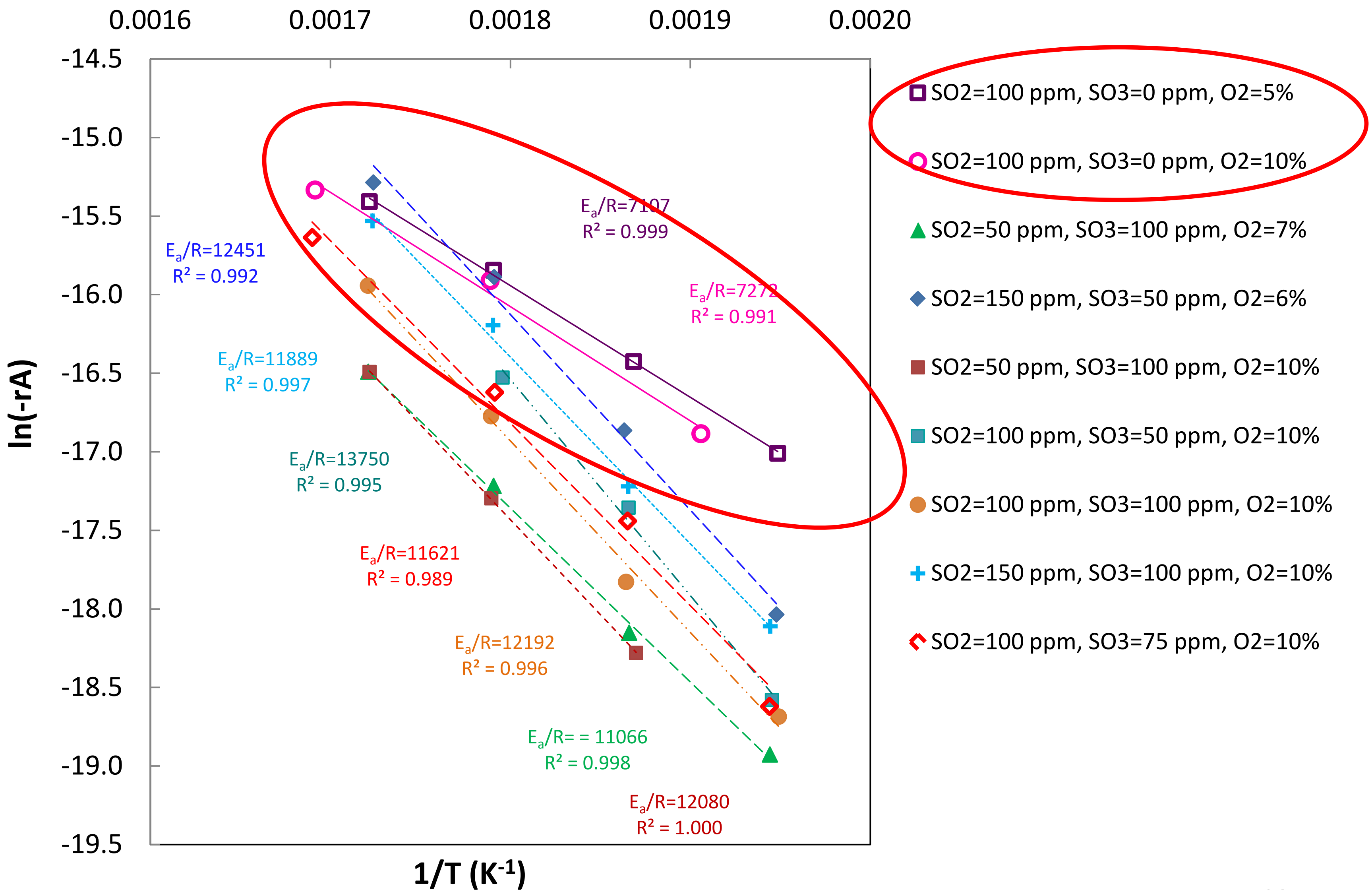
$$SO_2 + \frac{1}{2}O_2 \leftrightarrow SO_3 \qquad -r_{SO2} = k[SO_2]^{\alpha}[O_2]^{\beta}[SO_3]^{\gamma}$$



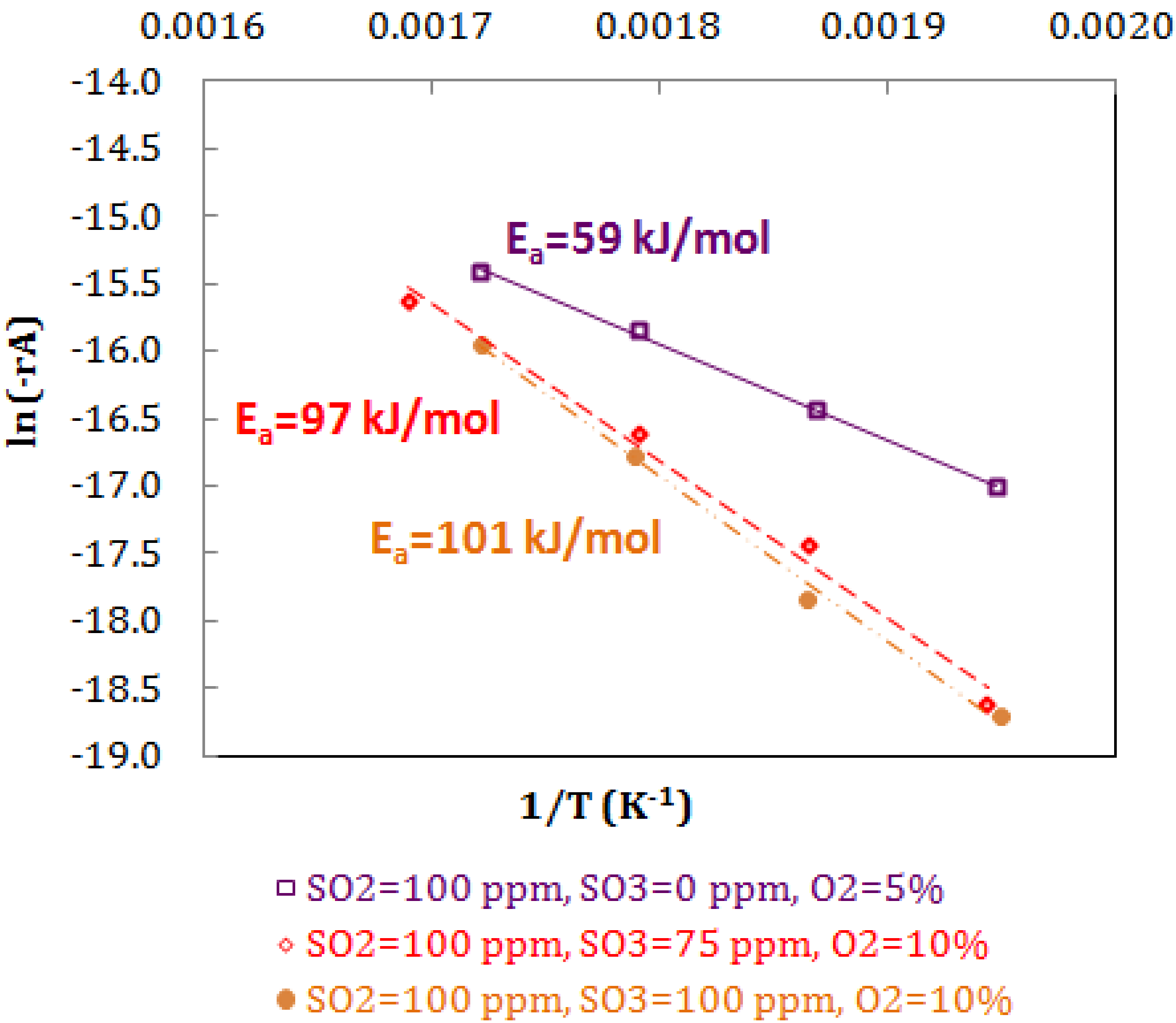
Activation energy



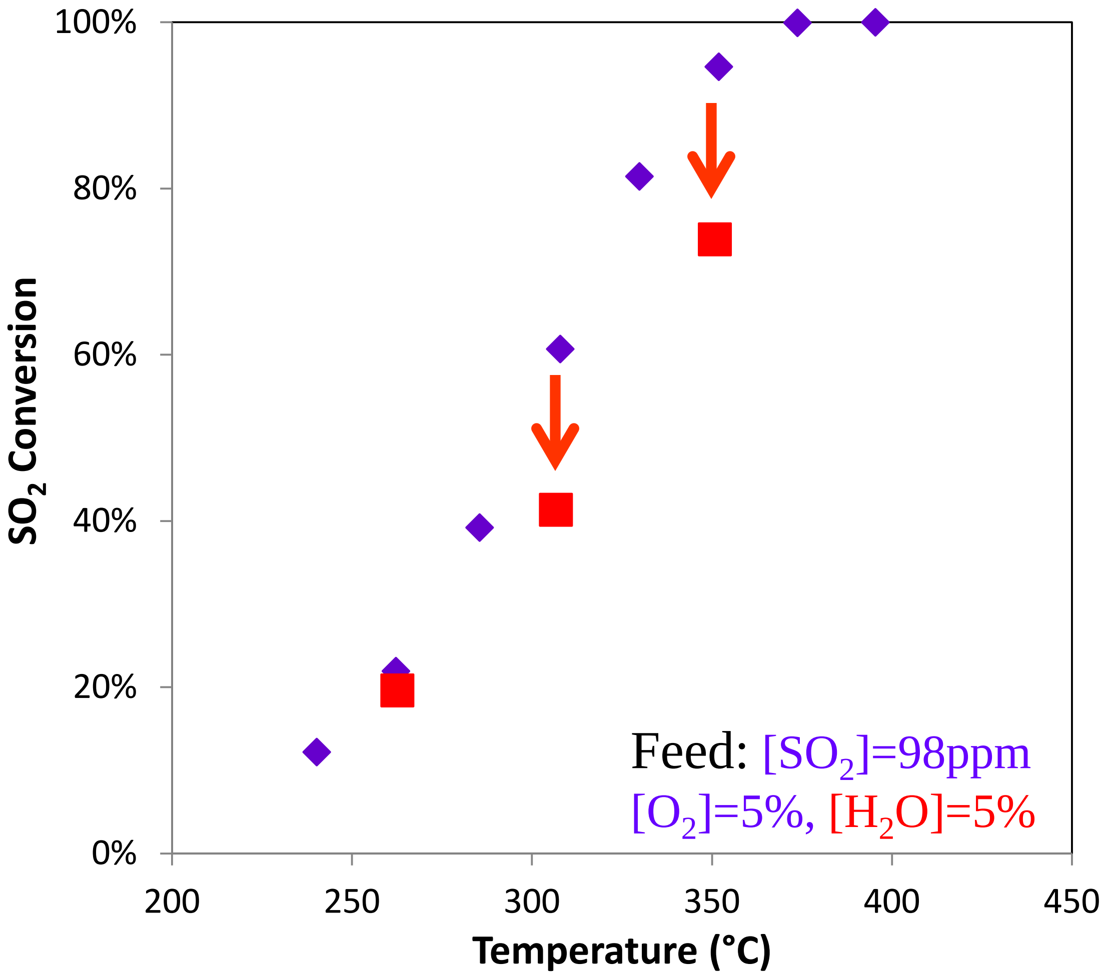
Activation energy



Effect of presence/absence of SO_3 on E_a

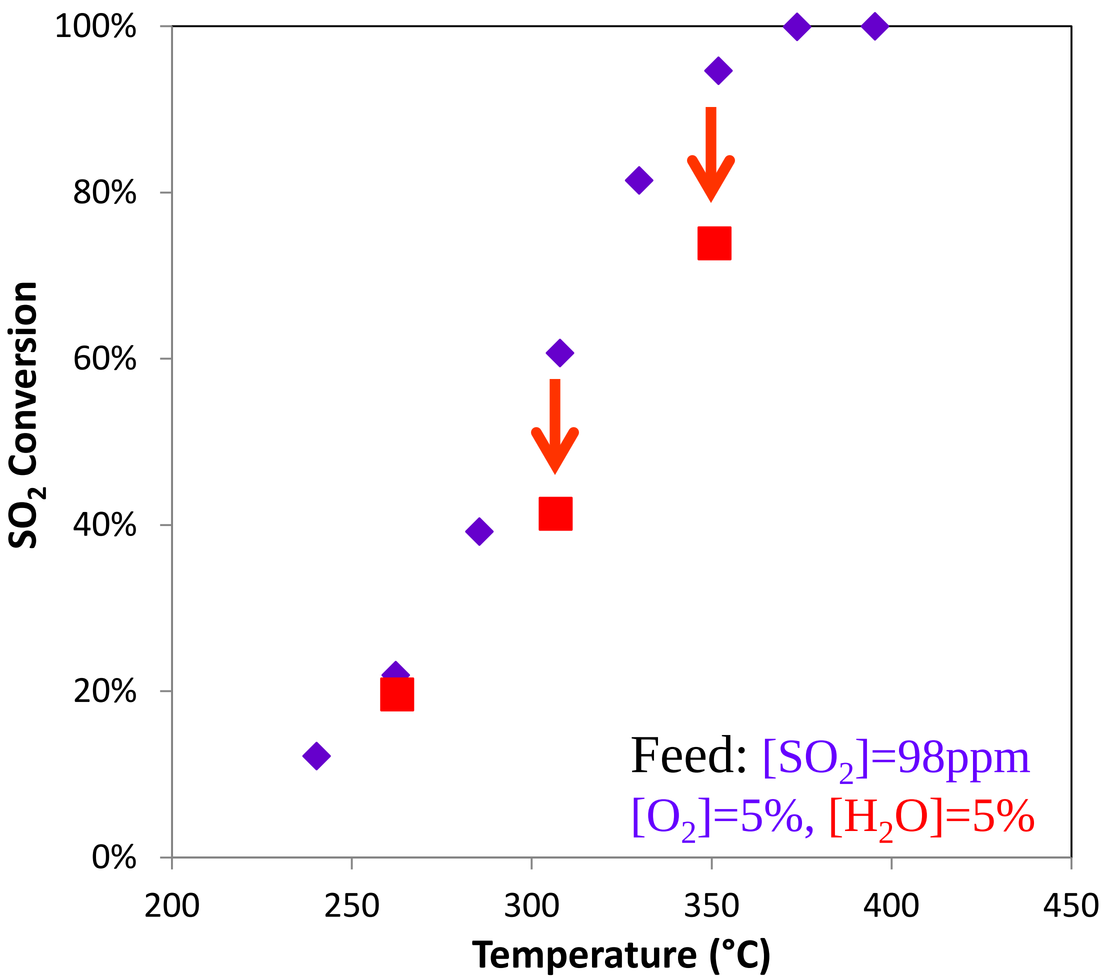


Effect of water



T (°C)	SO_2 Conversion	
	no water	5% water
262	21.9%	19.6%
307	60.7%	41.4%
351	94.7%	73.9%

Effect of water



T (°C)	SO_2 Conversion	
	no water	5% water
262	21.9%	19.6%
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351	94.7%	73.9%

At 351C:
SO_2 out = 25 ppm
SO_3 out = 1.4 ppm
H_2SO_4 out = 70 ppm

Model Set-up

- Differential data (high temperature guided by thermo)
- Assumed isothermal ($\Delta H_{SO2 \rightarrow SO3}$ mildly exothermic)
- Assumed steady state
- Objective function: $norm = \left(\frac{1}{num\_datapts}\right) * \sqrt{sum\left(\log^2\left(\frac{X_{\exp}}{X_{model}}\right)\right)}$
- First, each reaction optimized individually without altering other rates

1) $SO_2 + * \leftrightarrow SO_2^*$ --- (1,2)

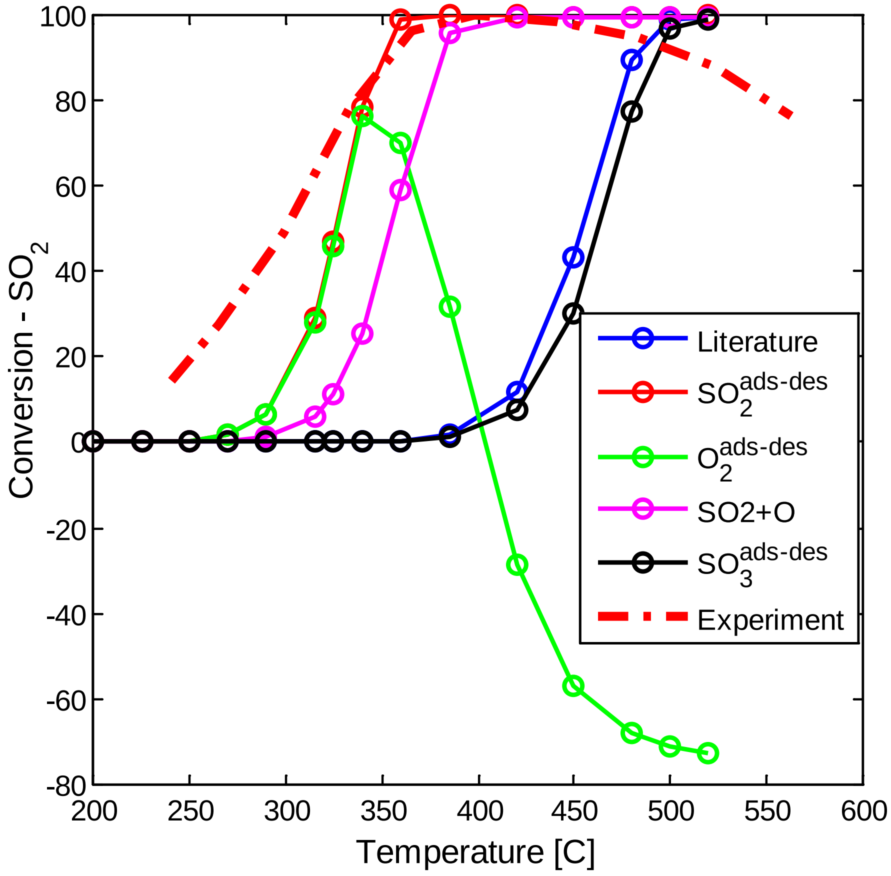
2) $O_2 + 2* \leftrightarrow 2O^*$ --- (3,4)

3) $SO_2^* + O^* \leftrightarrow SO_3^*$ --- (5,6)

4) $SO_3^* \leftrightarrow SO_3 + *$ --- (7,8)

$$-r_{SO_2} = \frac{k_{3f} K_1 \sqrt{K_2}[SO_2][O_2]^{0.5}}{1 + \sqrt{K_1}[SO_2] + \sqrt{K_2}[O_2]^{0.5} + \frac{1}{K_4}[SO_3]}(1-\beta)$$

Comparison of individual reaction optimization

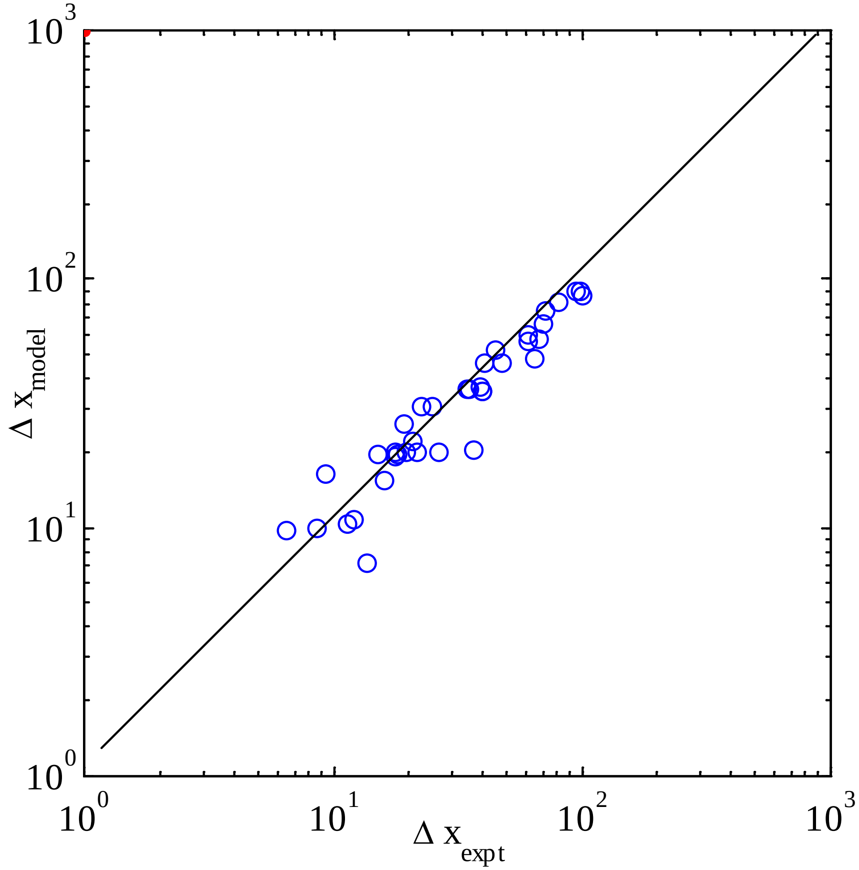


Reaction optimized	Objective function
Literature	1.743
SO_2 ads – des	0.278
O_2 ads – des	0.309
SO_2*+O* (fwd-rev)	0.528
SO_3 ads – des	1.70

Model suggests the rate is highly sensitive to SO_2 and O_2 adsorption-desorption kinetics, and some to surface rxn

Further optimization

Since the model suggests the rate is highly sensitive to SO_2 and O_2 adsorption-desorption kinetics, parameters from these reaction steps were used for further optim.

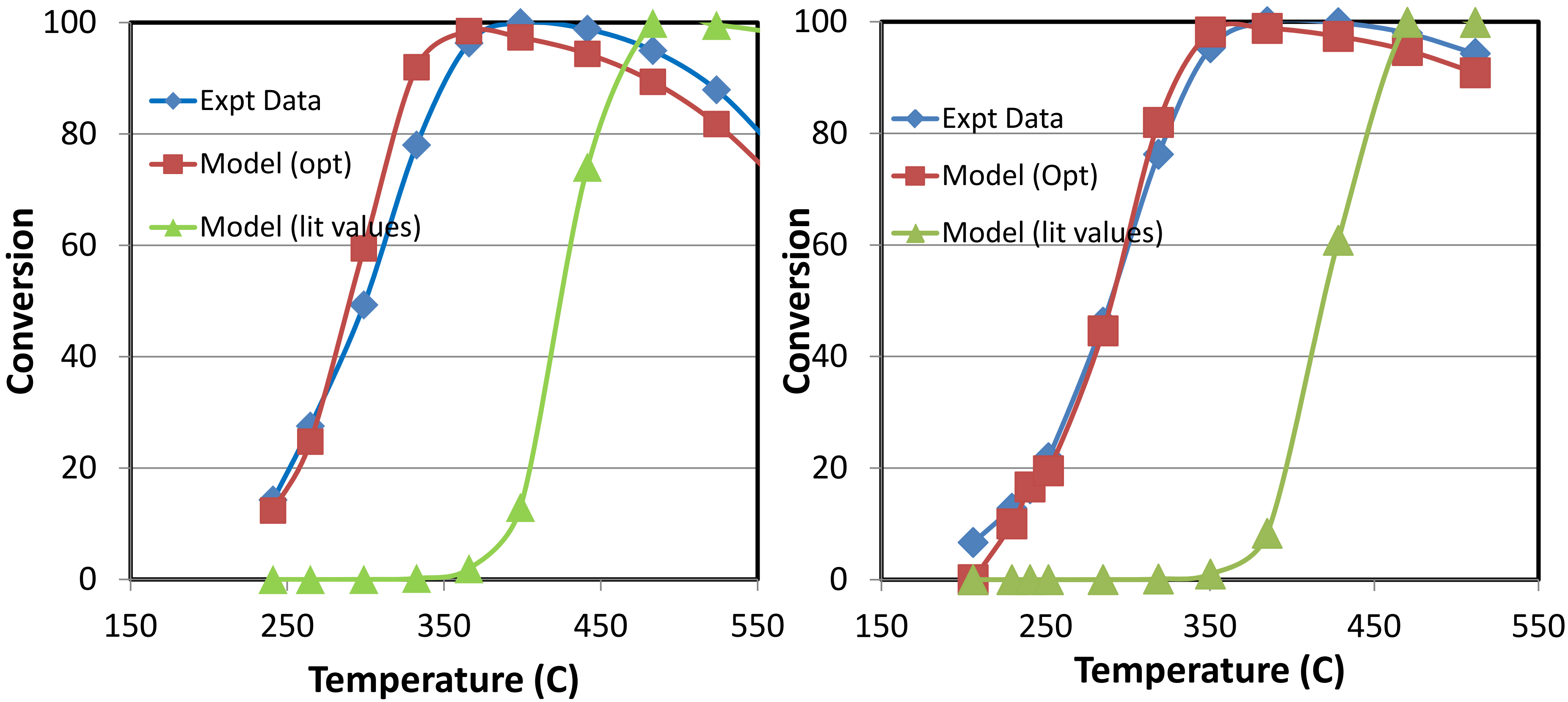


Optimized for reaction rates that showed highest norm variation - r_2, r_3, r_4, r_5, r_6

Optimized for rate parameters which showed maximum change - A_3, A_4, A_5, A_6, E_3

Reaction optimized	**Objective function**
Literature	1.743
A_3,A_4,A_5,A_6,E_3	0.0375

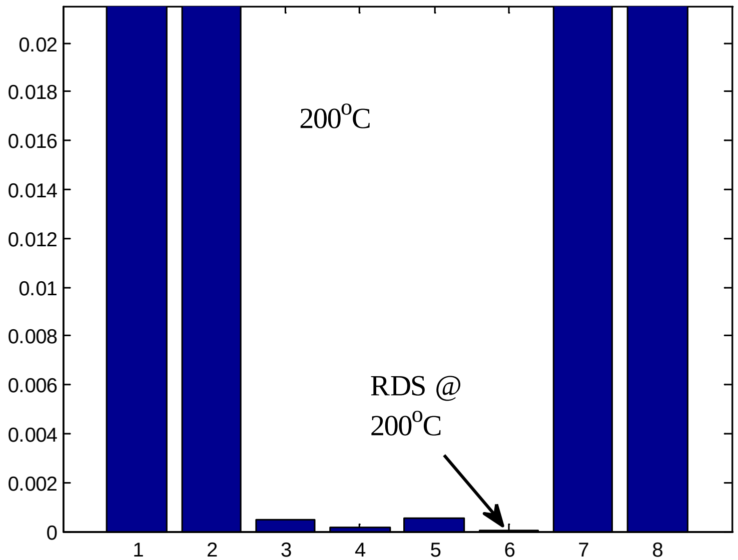
Modeling validation

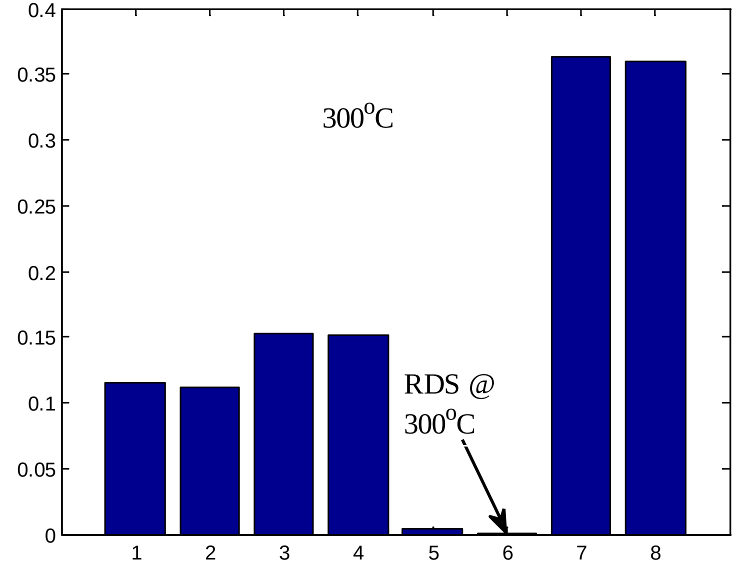


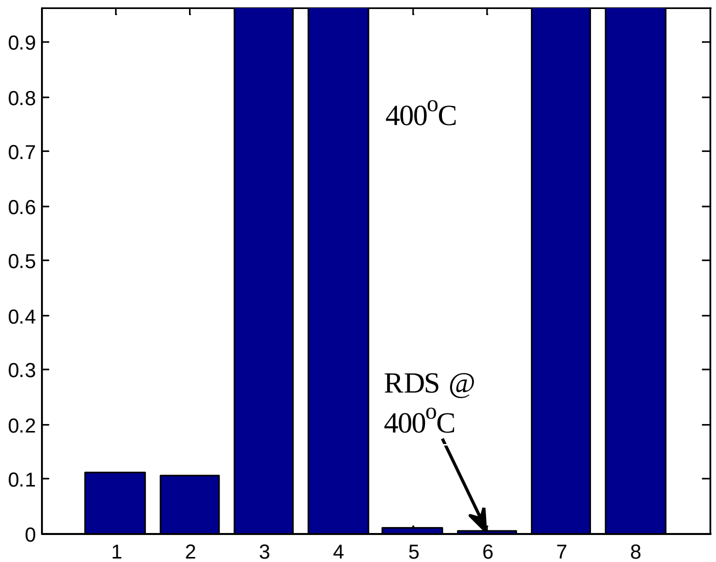
SO_2 = 100 ppm, SO_3 = 75 ppm, O_2 = 10%
SV = 25000 h^{-1}

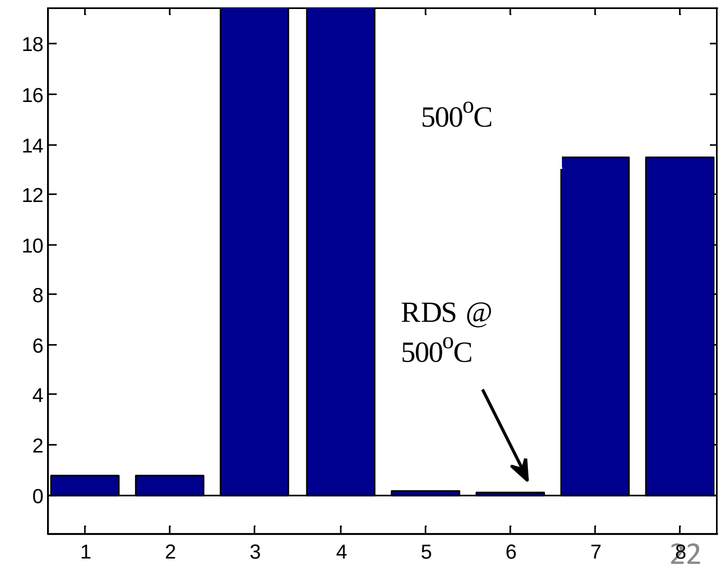
SO_2 = 200 ppm, SO_3 = 0 ppm, O_2 = 10%
SV = 25000 h^{-1}

Modeling RDS

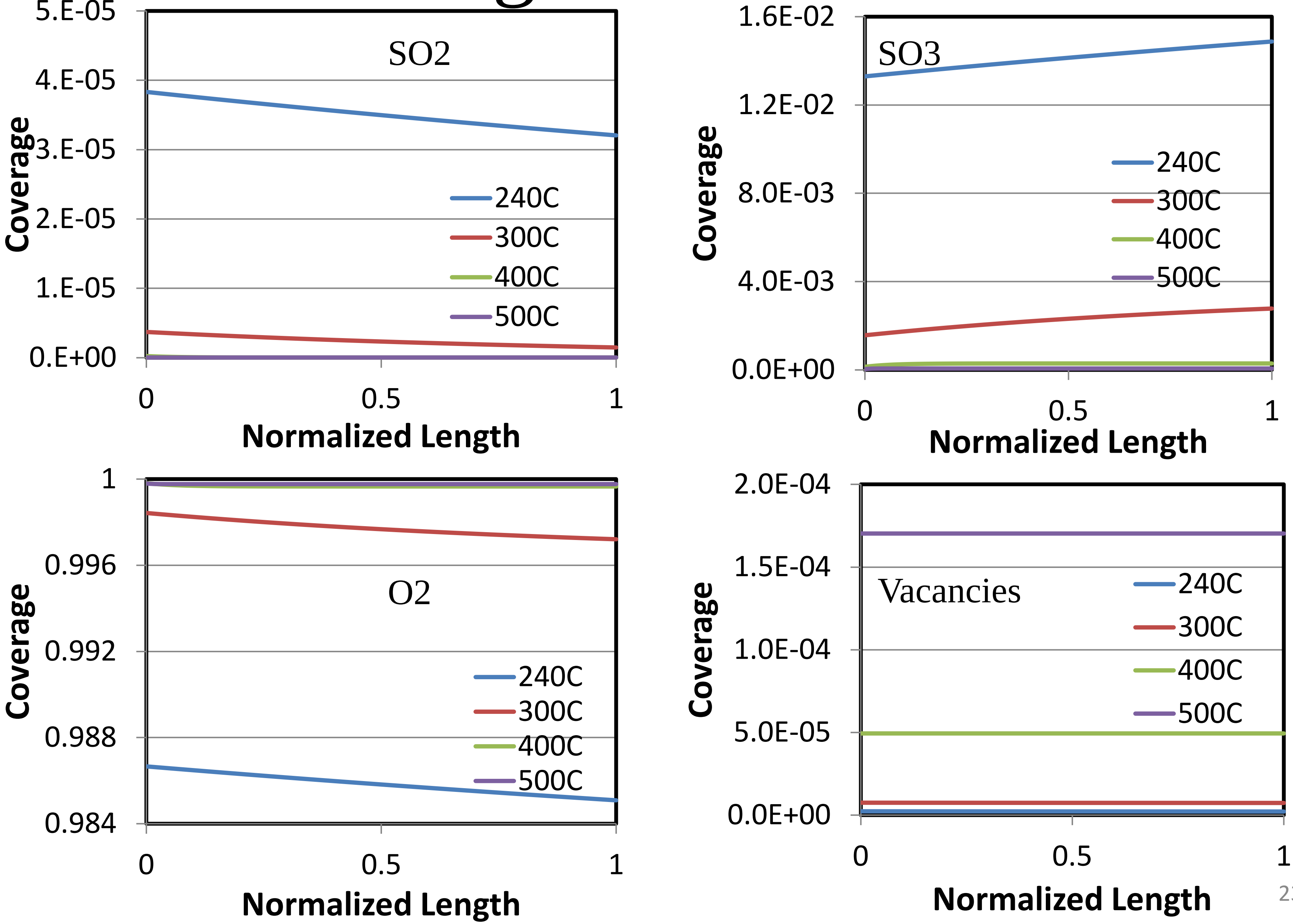








Surface coverages



Conclusions

- DOC readily converts $SO_2 \rightarrow SO_3$
  - T > 225°C
- SO_3 and O_2 inhibit the reaction
- Modeling suggests that the reaction is quite sensitive to O_2 and SO_2 adsorption/desorption kinetics, but that the surface reaction ($SO_2 + O \rightarrow SO_3$) is rate determining.

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  - $T > 225°C$
- SO_3 and O_2 inhibit the reaction
- Modeling suggests that the reaction is quite sensitive to O_2 and SO_2 adsorption/desorption kinetics, but that the surface reaction ($SO_2 + O \rightarrow SO_3$) is rate determining.
- In other words we don't know much yet
- Somewhat Déjà-Vu with NO oxidation kinetics

Acknowledgements

- Thanks to Cummins for financial support
- Thanks to JM for catalyst samples