Remaining Challenges to the Commercialization of Hydrocarbon Selective Reduction (HC-SCR) of NOx on Ag Catalysts.

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Two main issues:

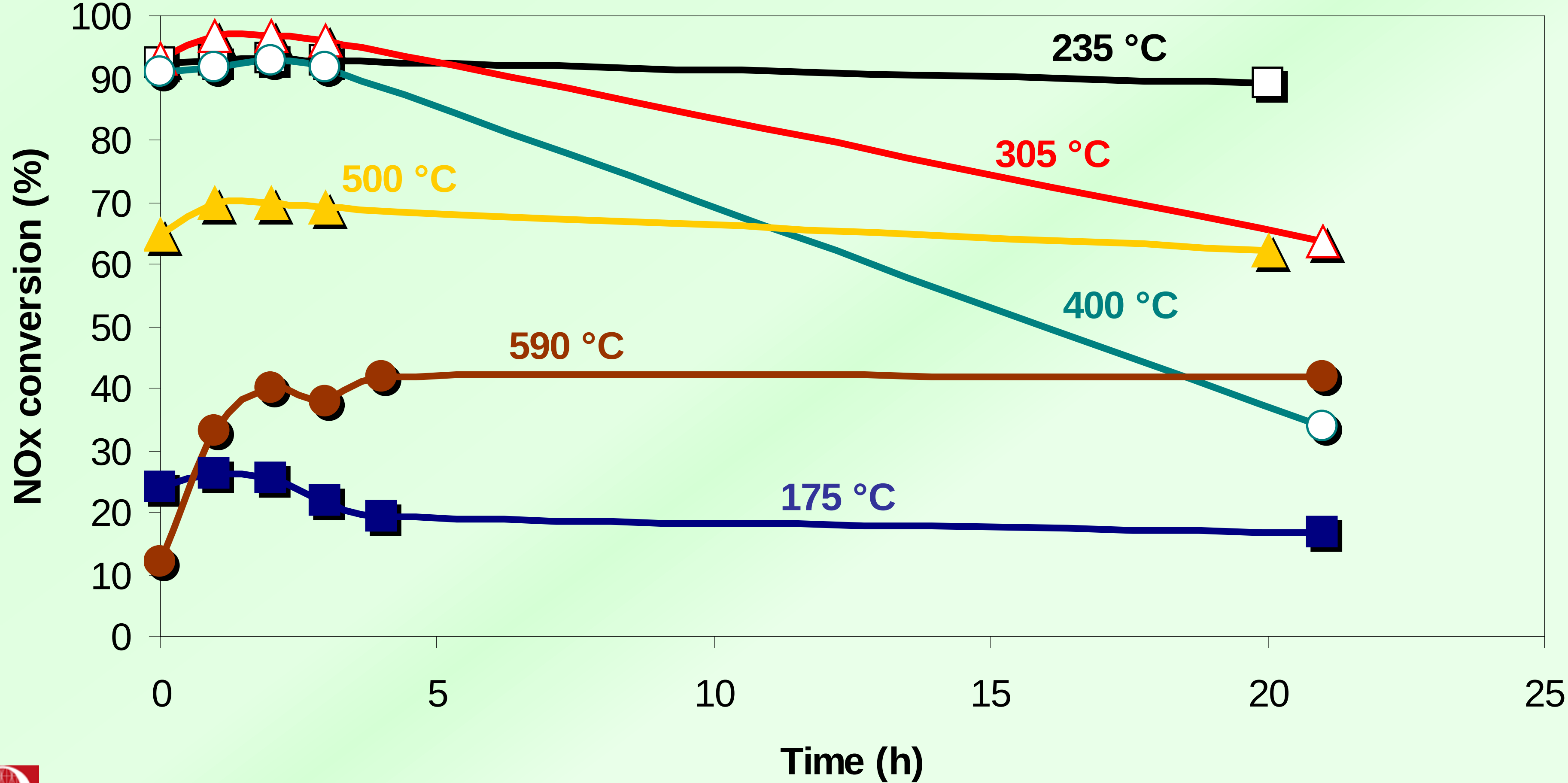
sensitivity to sulfur;

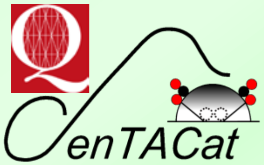
need to reduce activity loss, and examine regeneration options.

limited low temperature activity;

change the reductant;
modify the catalyst preparation;
investigate the reaction mechanism;
use this knowledge to enhance performance.

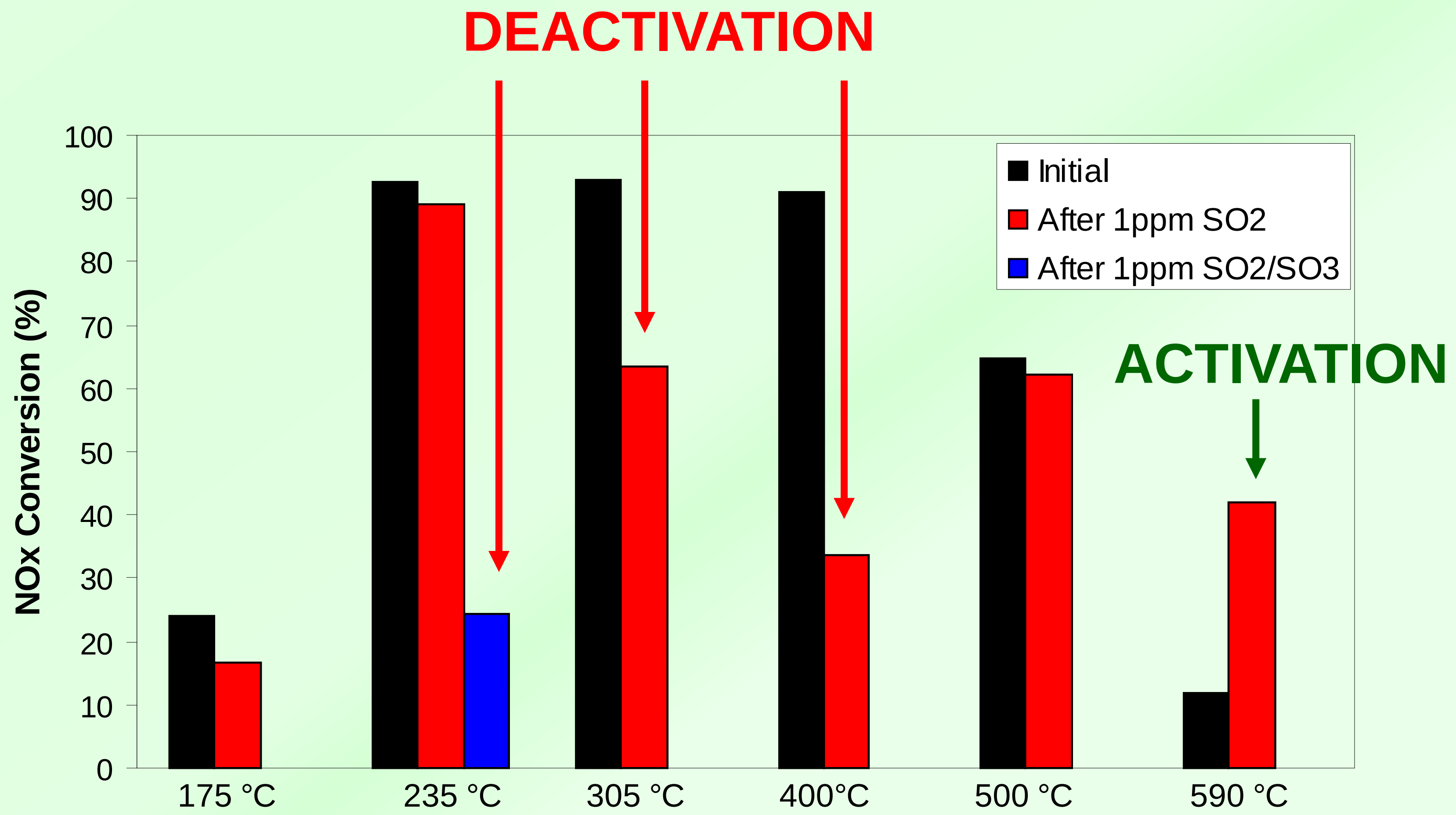
Effect of SOx on conversion of NOx after exposure to 1 ppm SO_2 at different reaction temperatures





Reaction Conditions: GHSV: 200,000 h^{-1}. NO, 720 ppm; SO_2, 1 ppm; O_2, 4.3%; CO_2, 7.2%; octane, 4340 ppm (as C_1); H_2O, 7.2%; H_2, 0.72%.

Deactivation due to SO_3 formation



Reaction Conditions: GHSV: 200,000 h^{-1}. NO, 720 ppm; SO_2 or SO_2/SO_3, 1 ppm; O_2, 4.3%; CO_2, 7.2%; octane, 4340 ppm (as C_1); H_2O, 7.2%.

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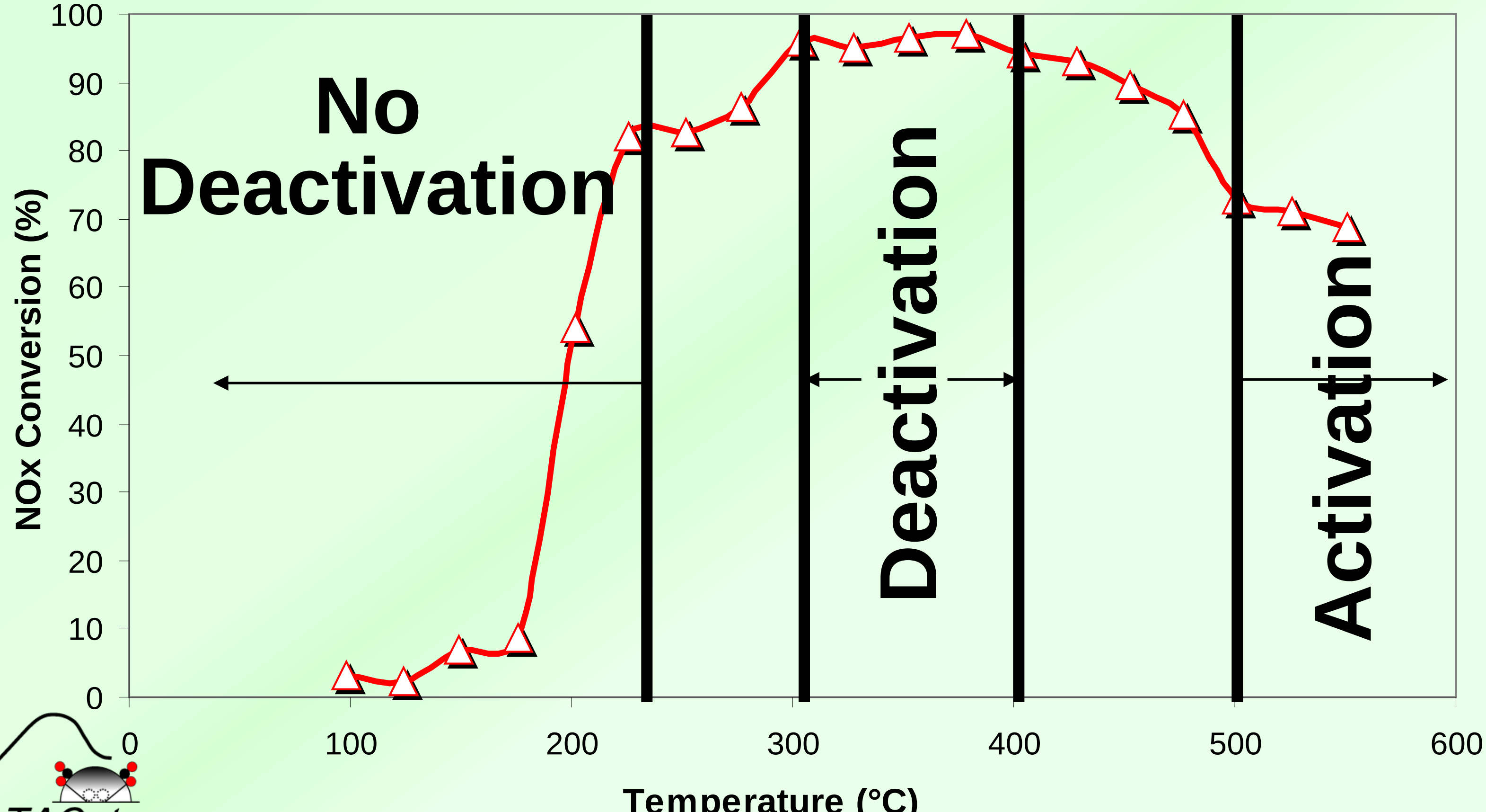
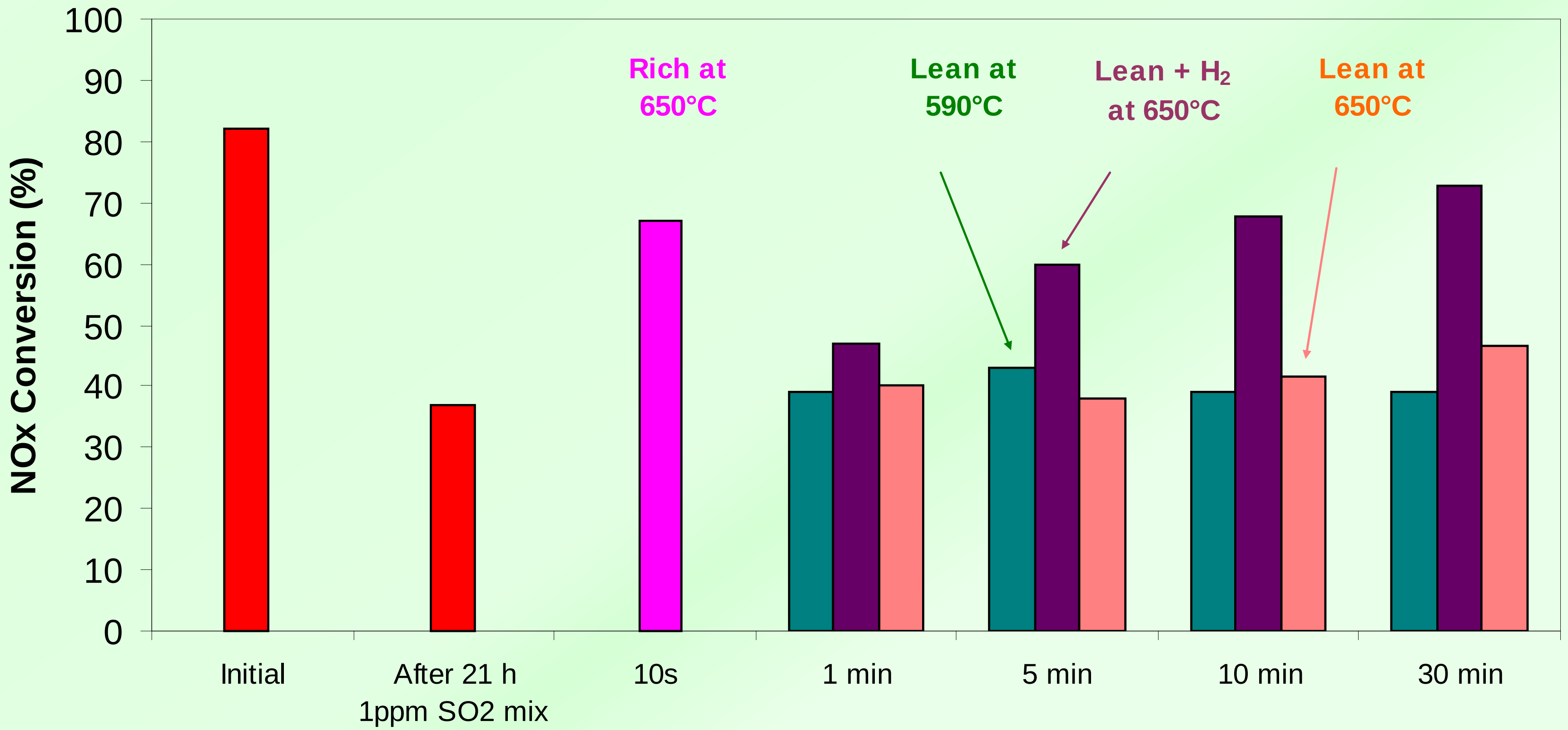
Zones of SO_2 effects

Meunier and Ross, Appl. Catal. B, 24 (2000) 23



Regeneration of sulphated catalysts – activity measured at 400 °C



Rich: CO, 1.5%; H_2, 0.5%; CO_2, 7.2%; H_2O, 7.2%

Lean: O_2, 4.3%; CO_2, 7.2%; H_2O, 7.2%

Lean + H_2: O_2, 4.3%; CO_2, 7.2%; H_2O, 7.2%; H_2, 0.72%

Improving sulfur tolerance by catalyst modification with base oxides

- **K. Yamamoto *et al*. (2006) modified Pt/TiO_2 by adding base oxide of Li, Na, K, Cs, Sr, Ba and La to improve the NO sorption capacity under SO_2-containing condition.**
- **They showed that SO_2 stored on Pt-Li_2O/TiO_2 was released at the lowest temperature under H_2 rich conditions.**

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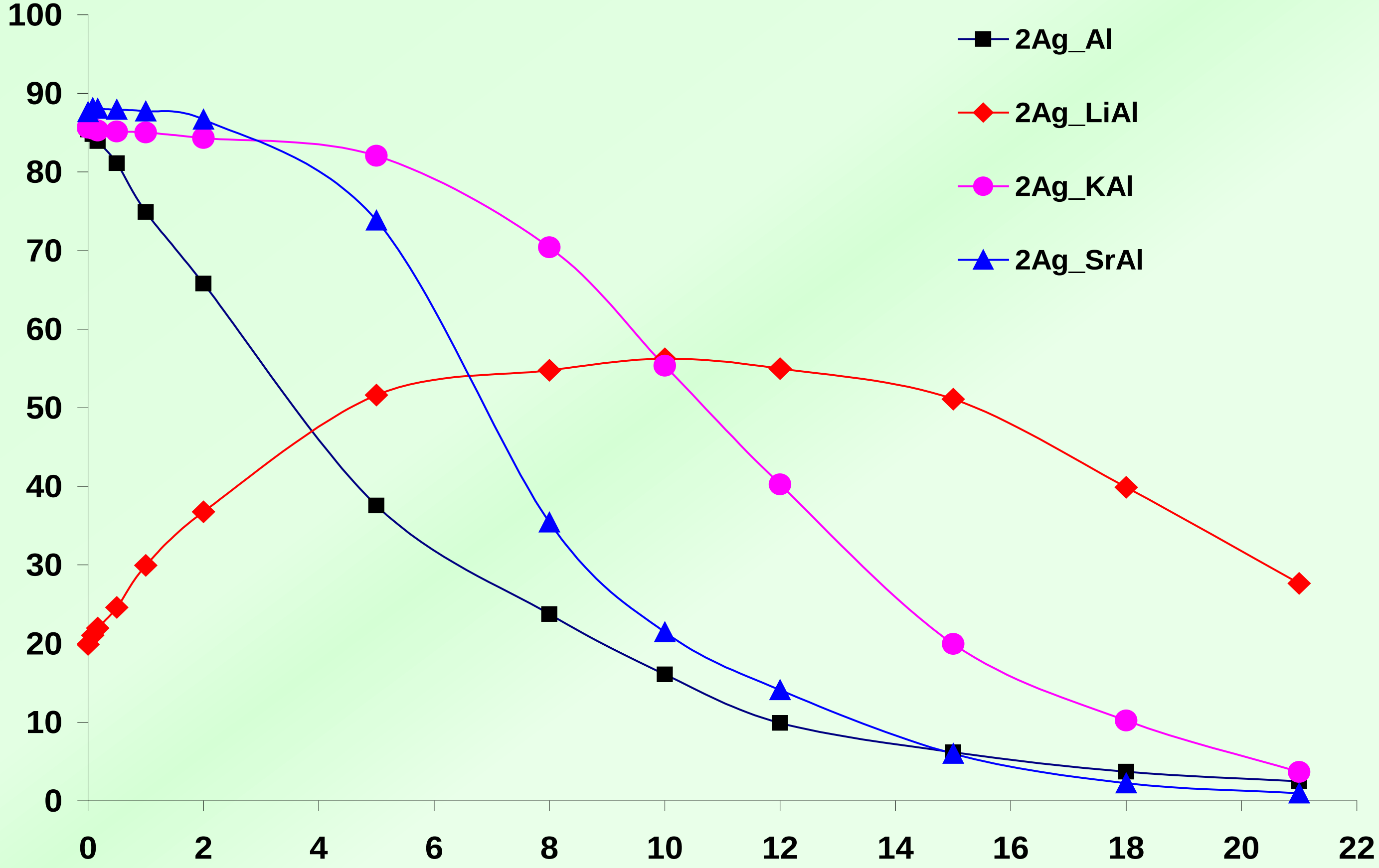
The Effect of 10 ppm SO_2 on Octane-SCR over Alkali-modified Ag Catalysts at 350 °C



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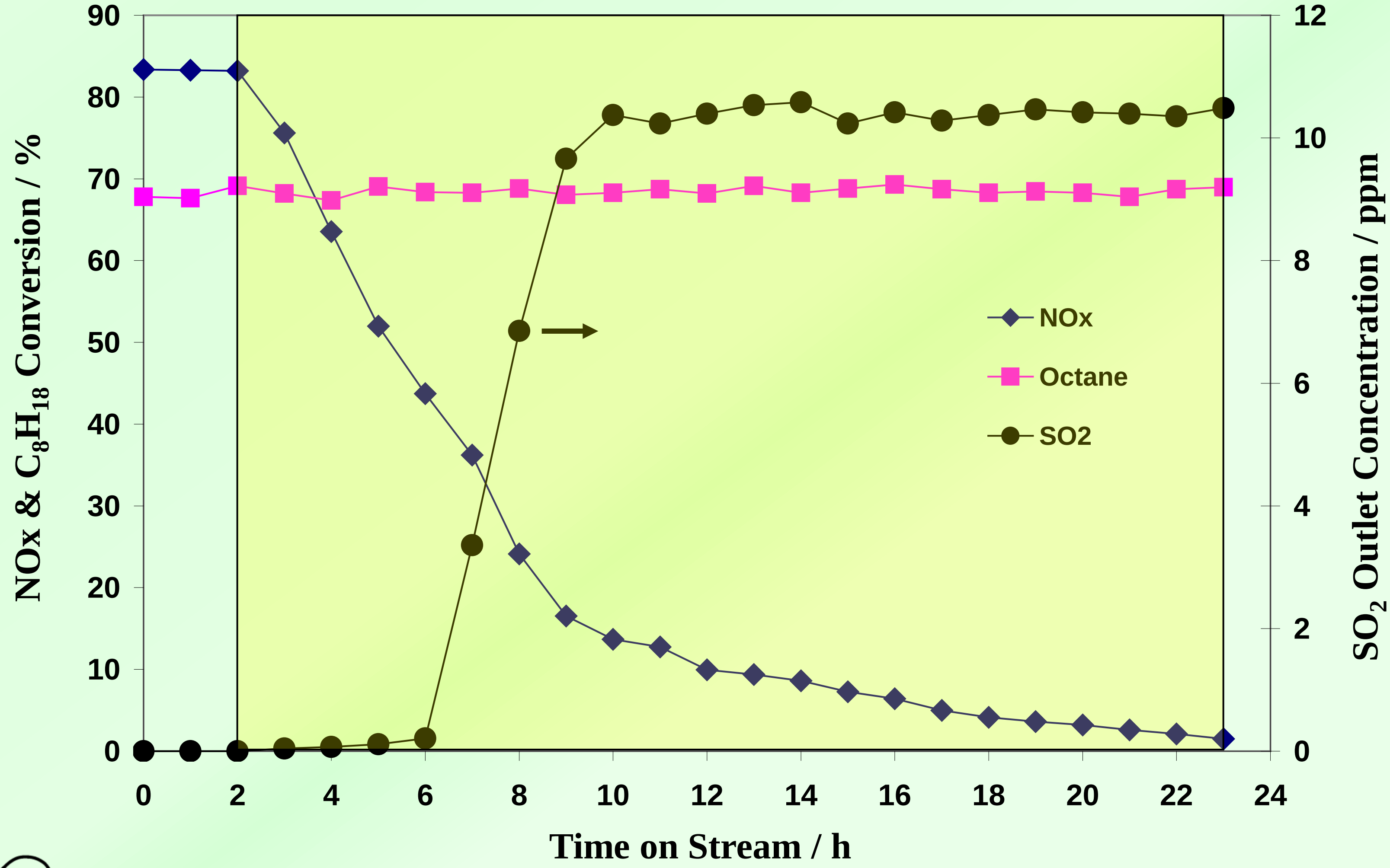
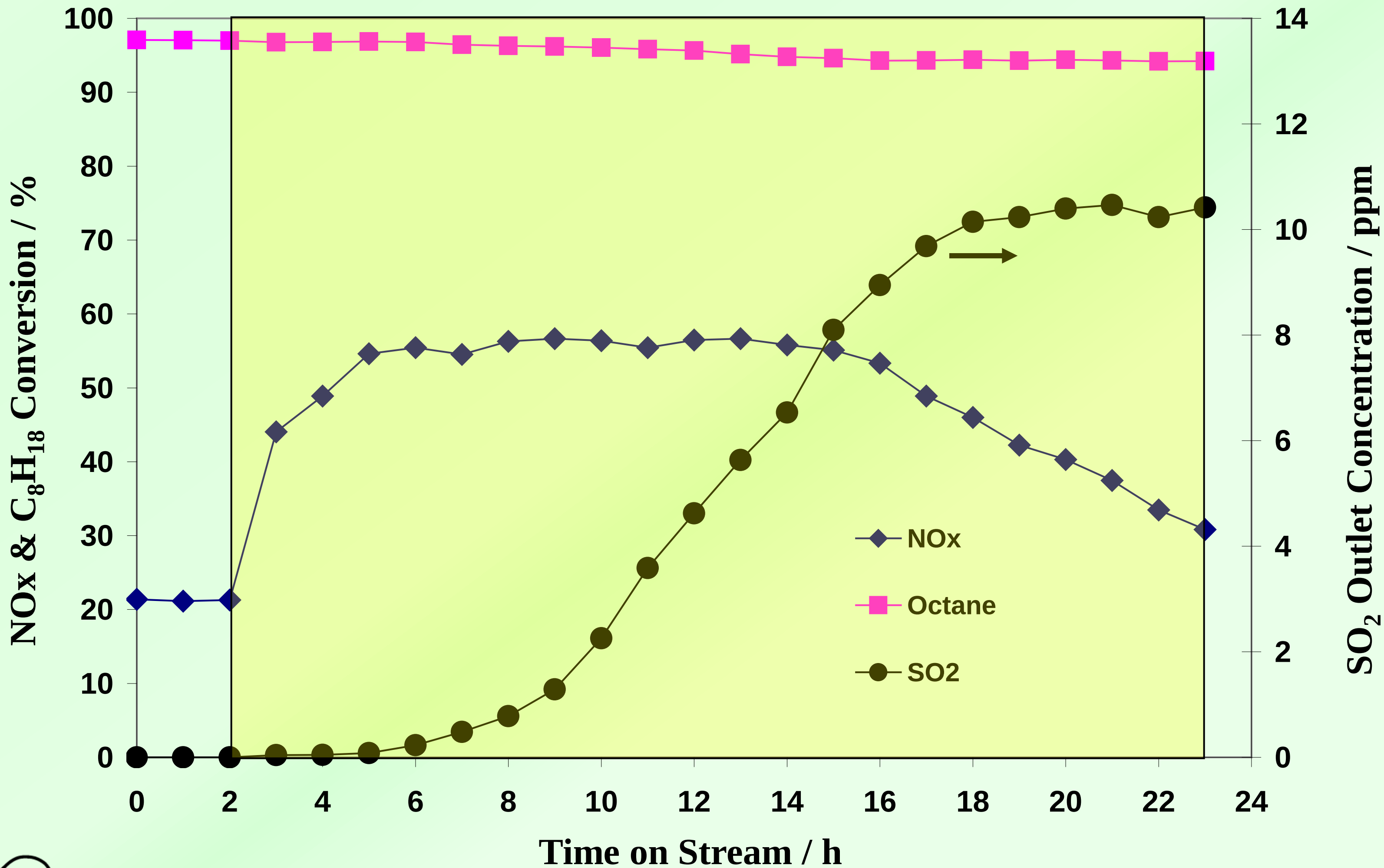
Alkali-modified catalysts capture much more sulfur

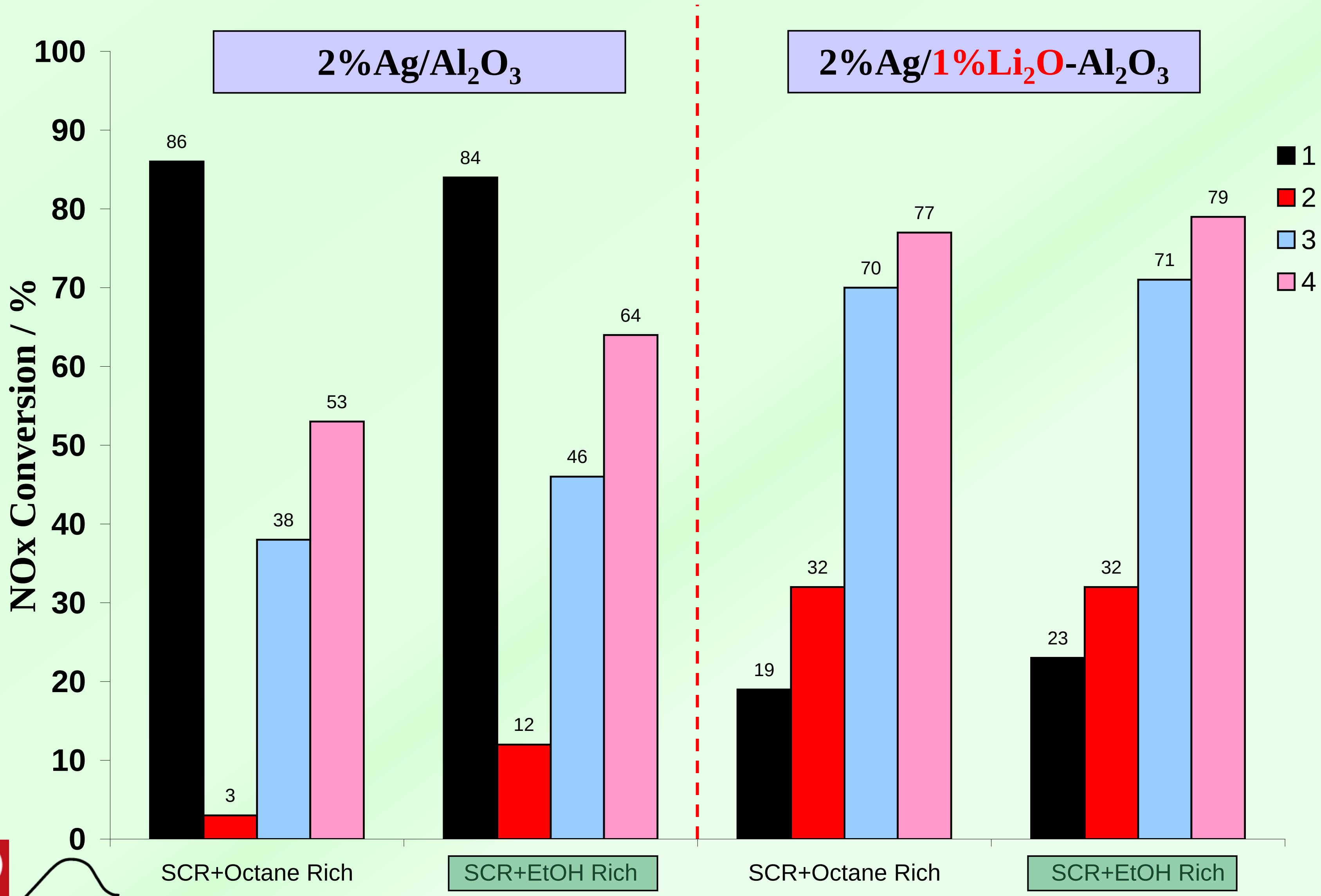
SO_x Stored in Ag/Al_2O_3 = 165 $\mu mol/g_{cat}$



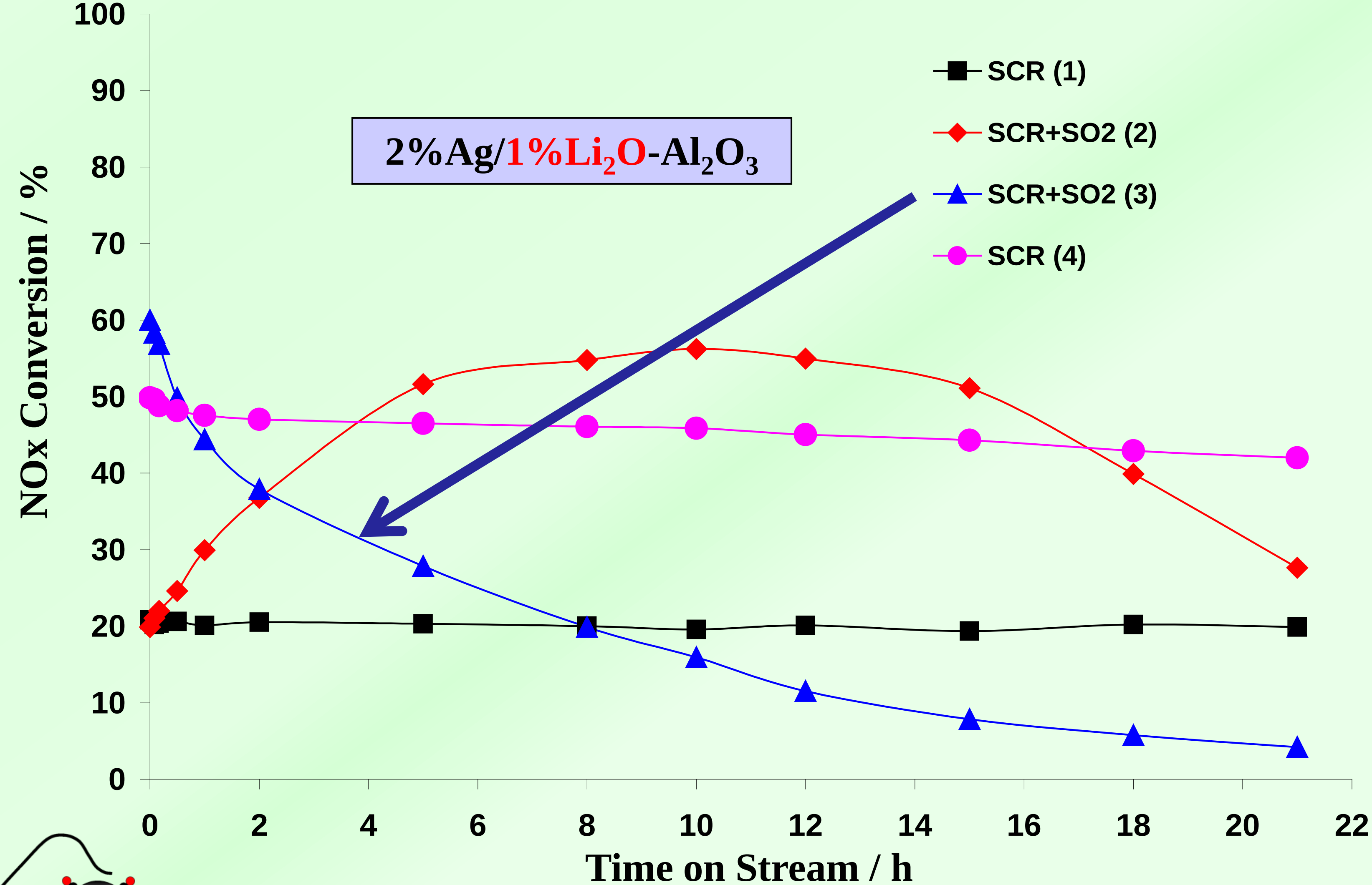
SO_x Stored in $Ag/X/Al_2O_3$ = 281 $\mu mol/g_{cat}$



Regeneration at 650 C



After regeneration, the activity declines "normally"



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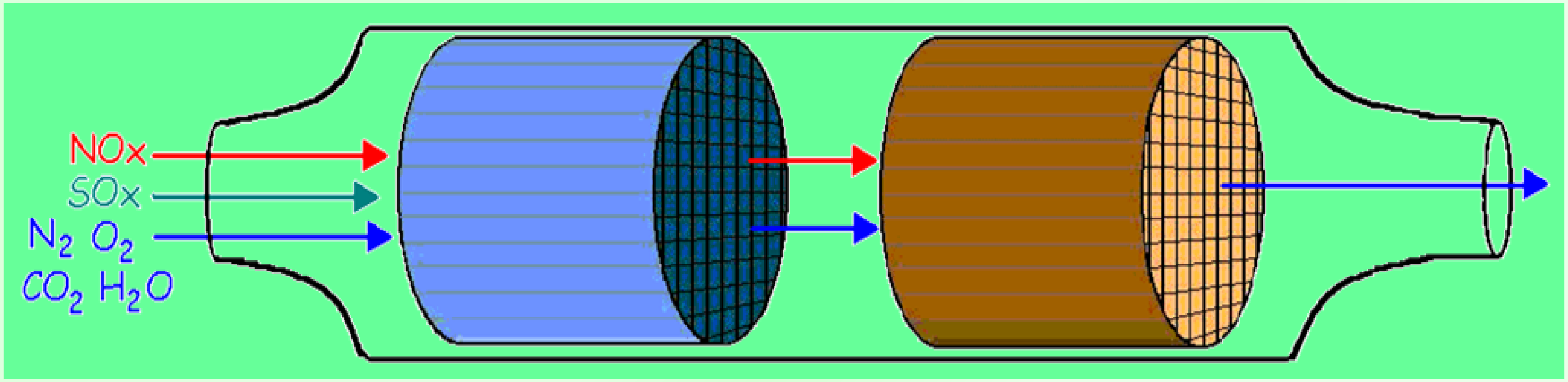
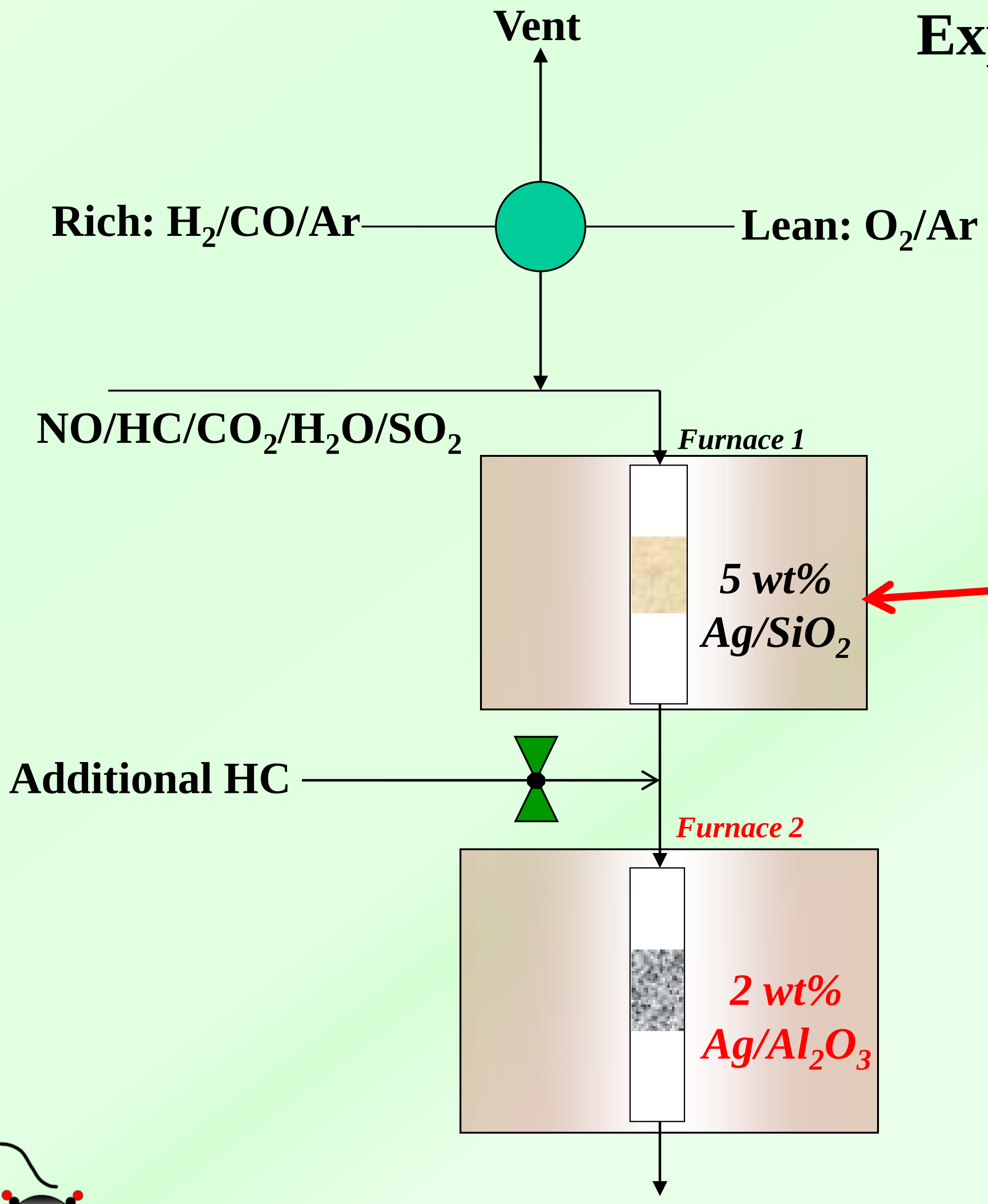
A possible solution

Use a regenerable SOx trap to protect the Ag/Al_2O_3



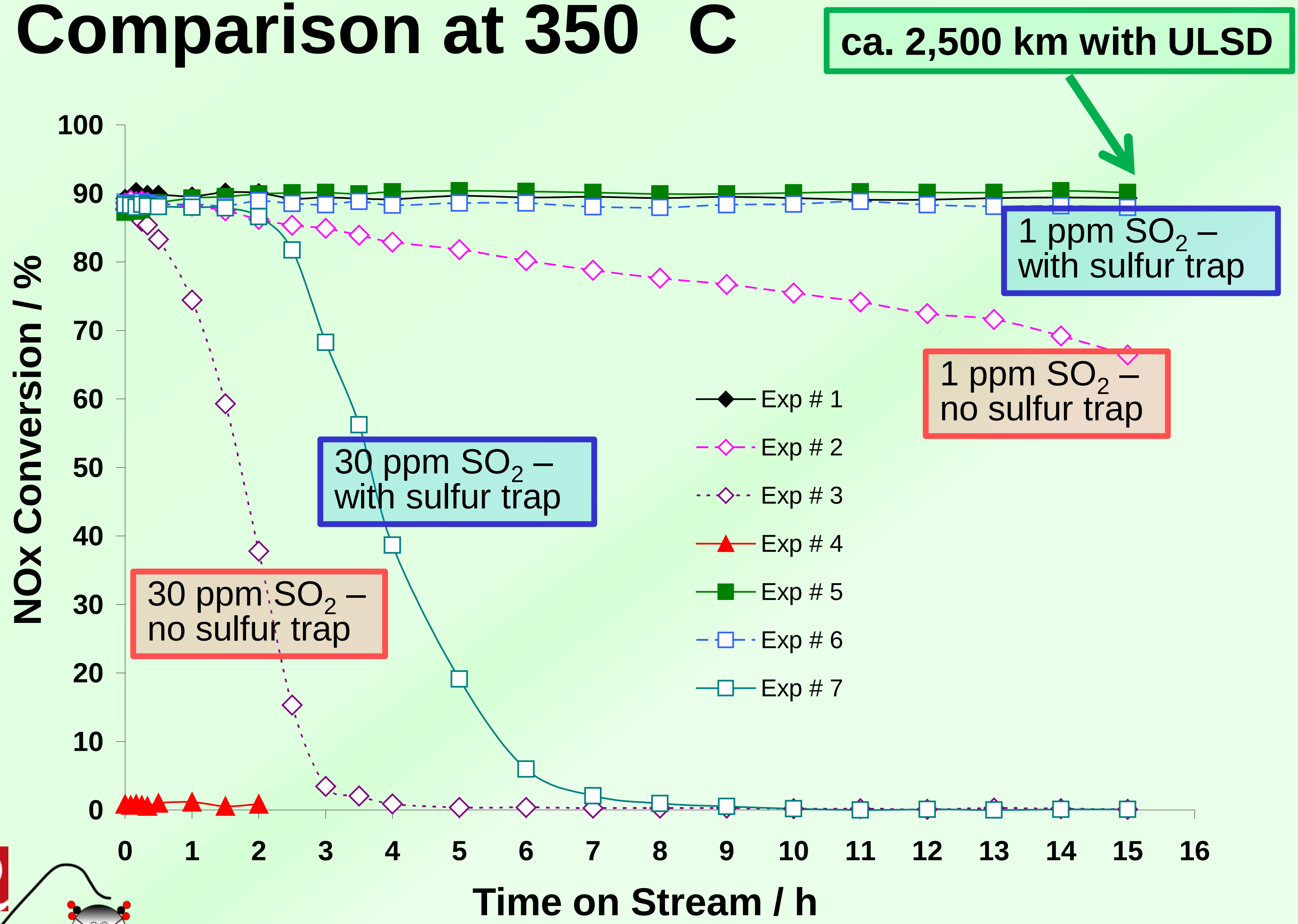
SOx trap **Ag/Al_2O_3**

Experimental Set Up



After: Liyu Li and David L. King
Appl. Catal. B: 100 (2010) 238.

Comparison at 350 C



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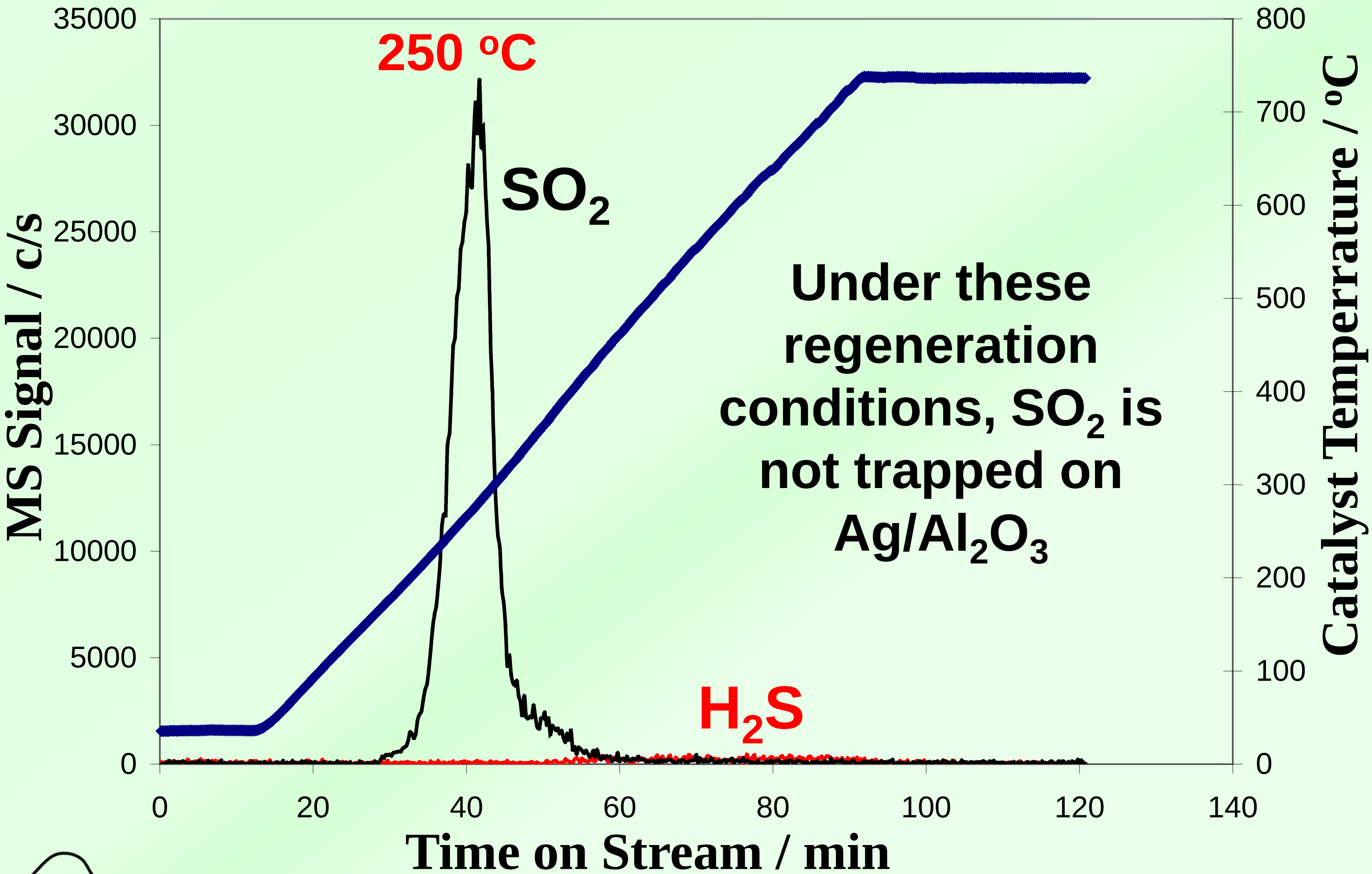
H_2-TPR shows SO_2 during regeneration



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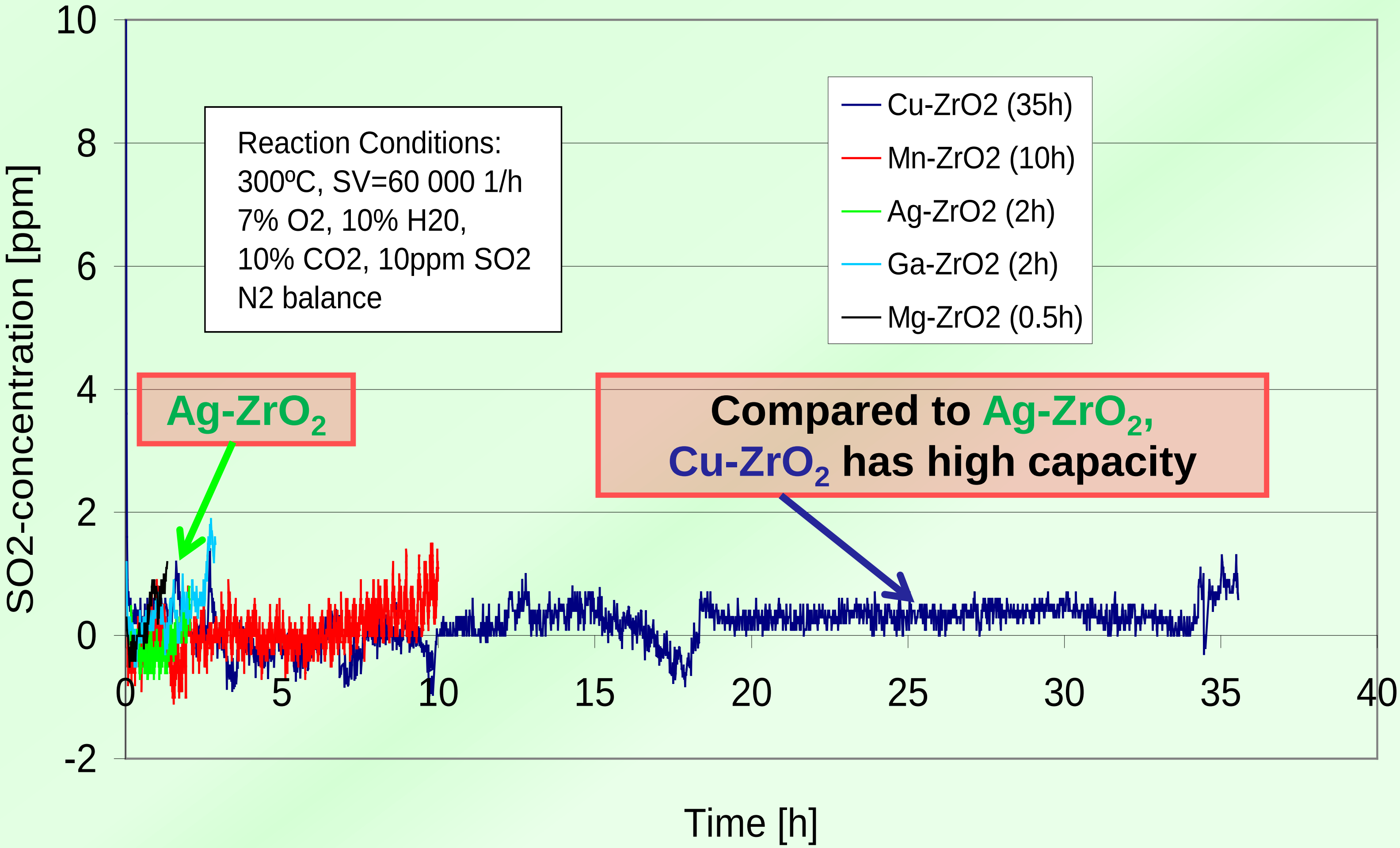
Alternative traps?
High capacity SOx traps based on ZrO_2



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Two main issues:

sensitivity to sulfur;

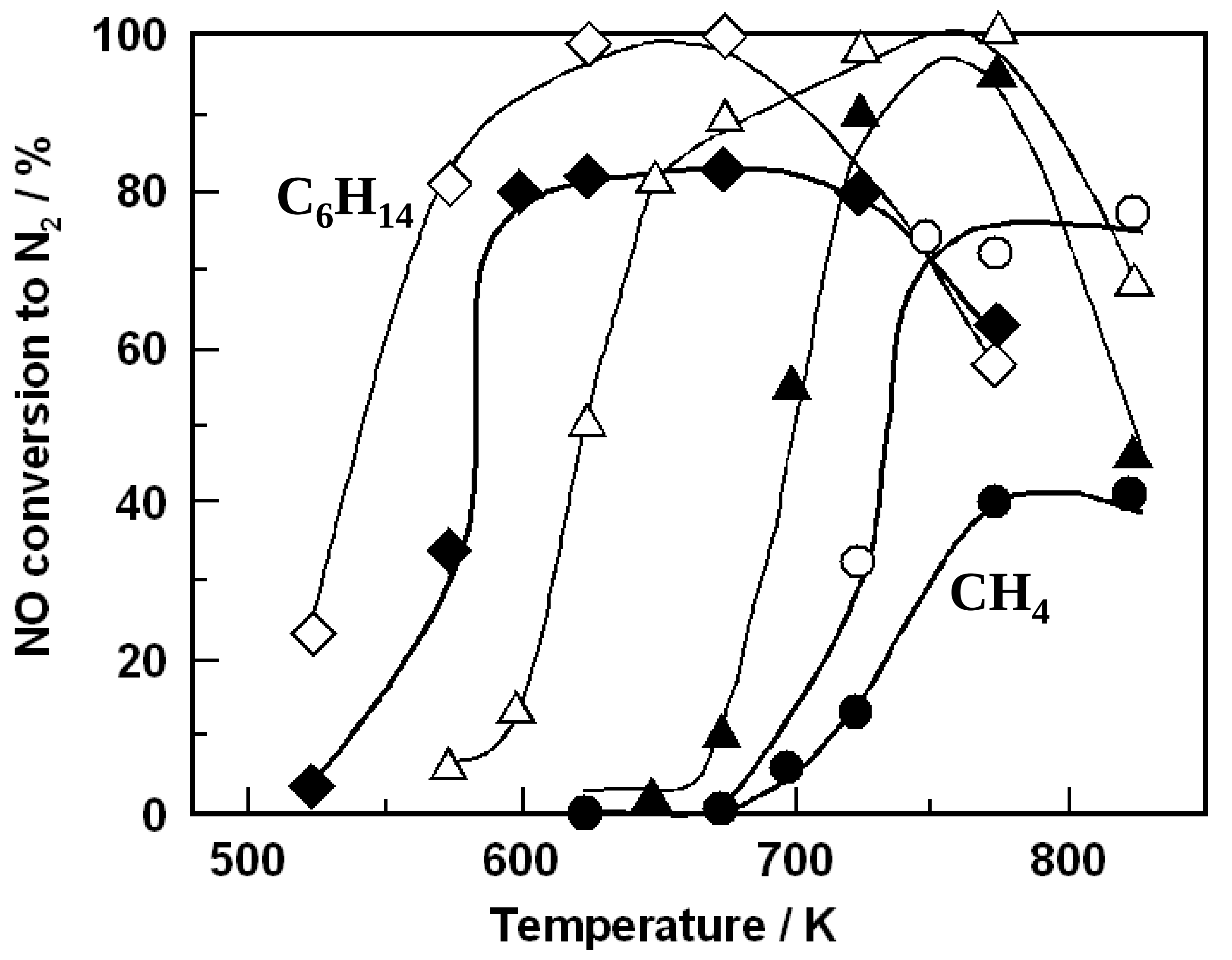
need to reduce activity loss, and examine regeneration options.

limited low temperature activity;

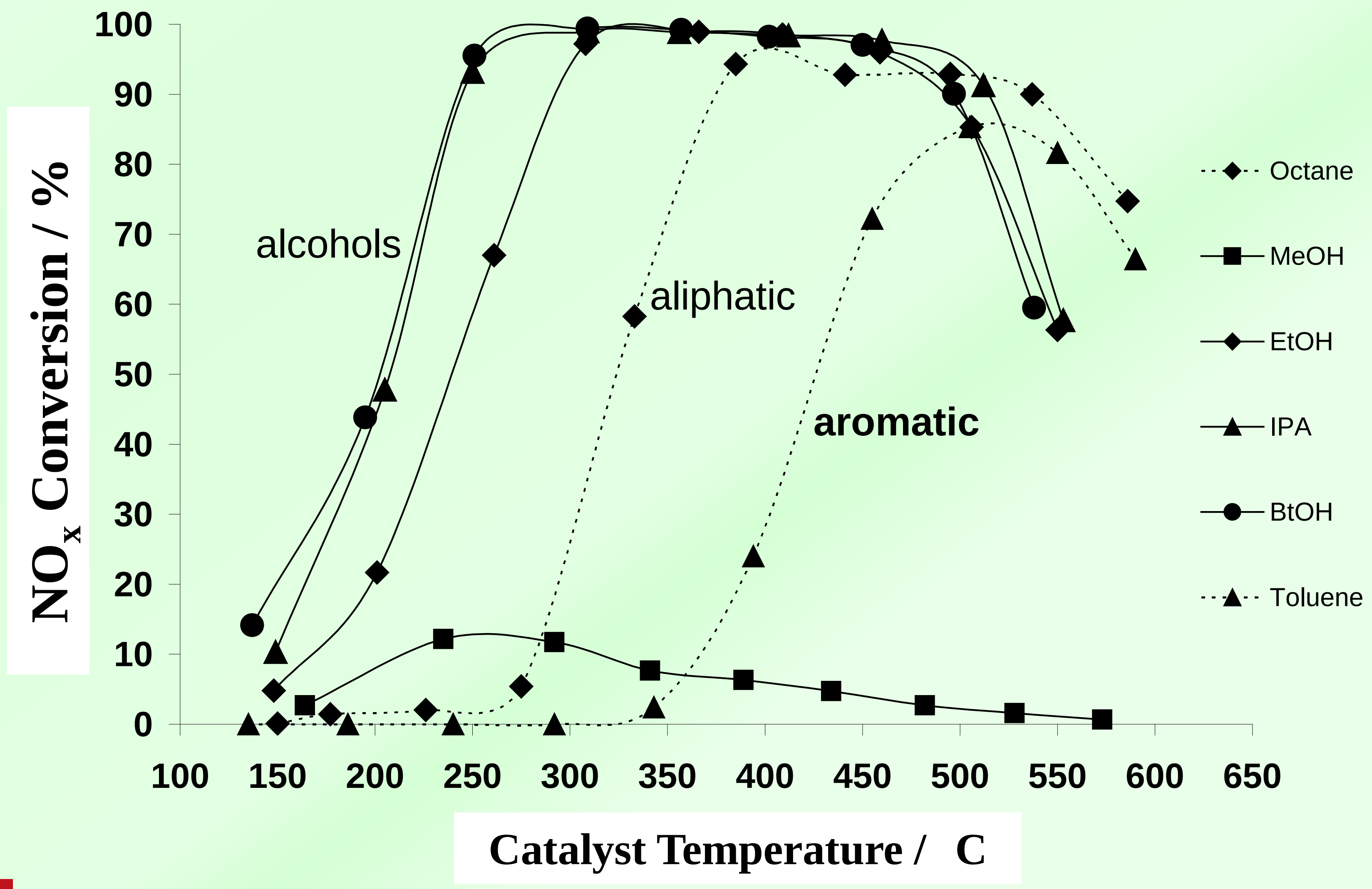
1. change the reductant;
2. modify the catalyst preparation;
3. investigate the reaction mechanism and use this knowledge to enhance performance.

1. Change the reductant

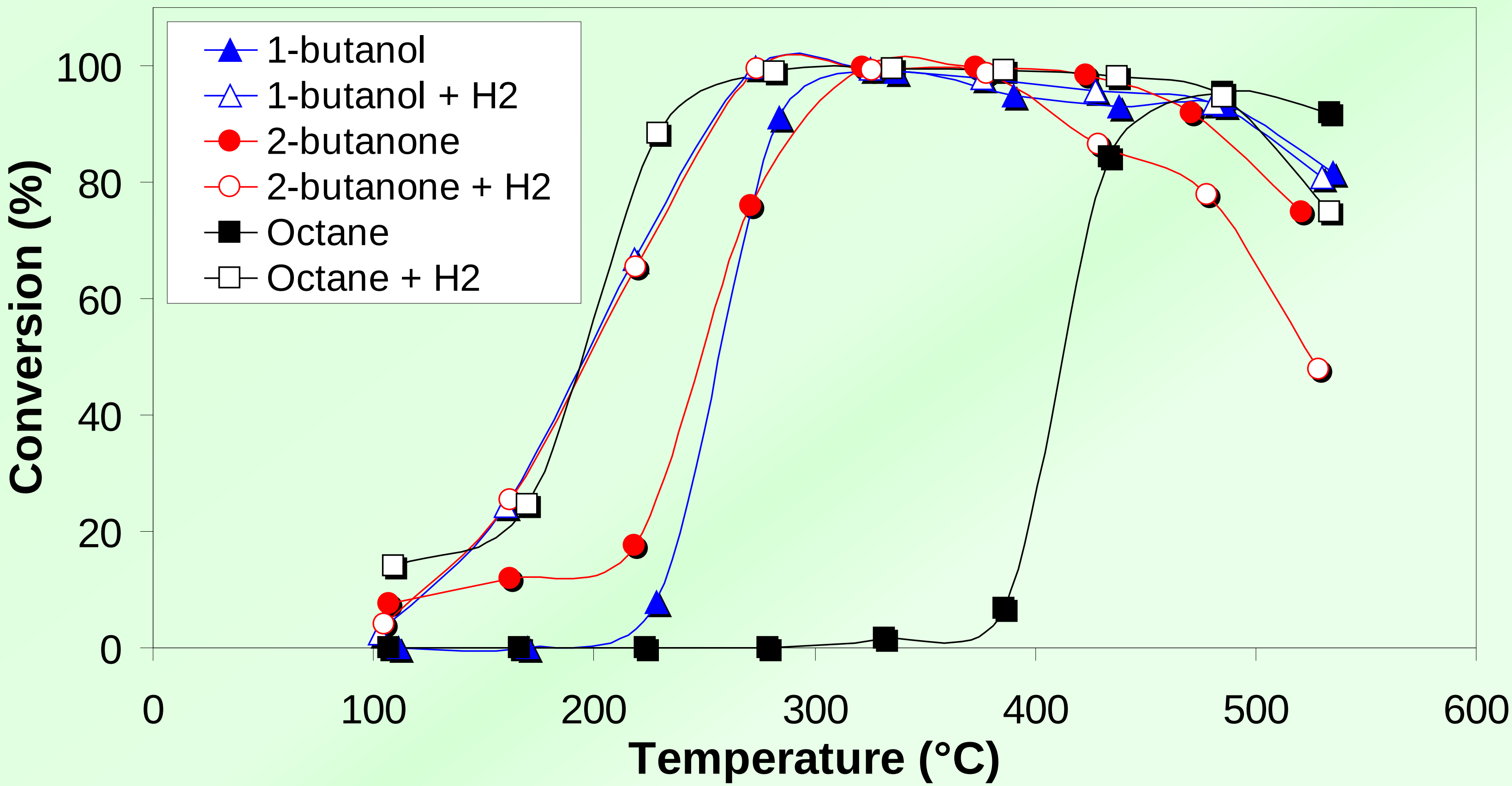
After Shimizu et al. Applied Catalysis B, 25 (2000) 239.



Functionalized reductants are much more active



Functionalized reductants are also more effective on addition of H_2



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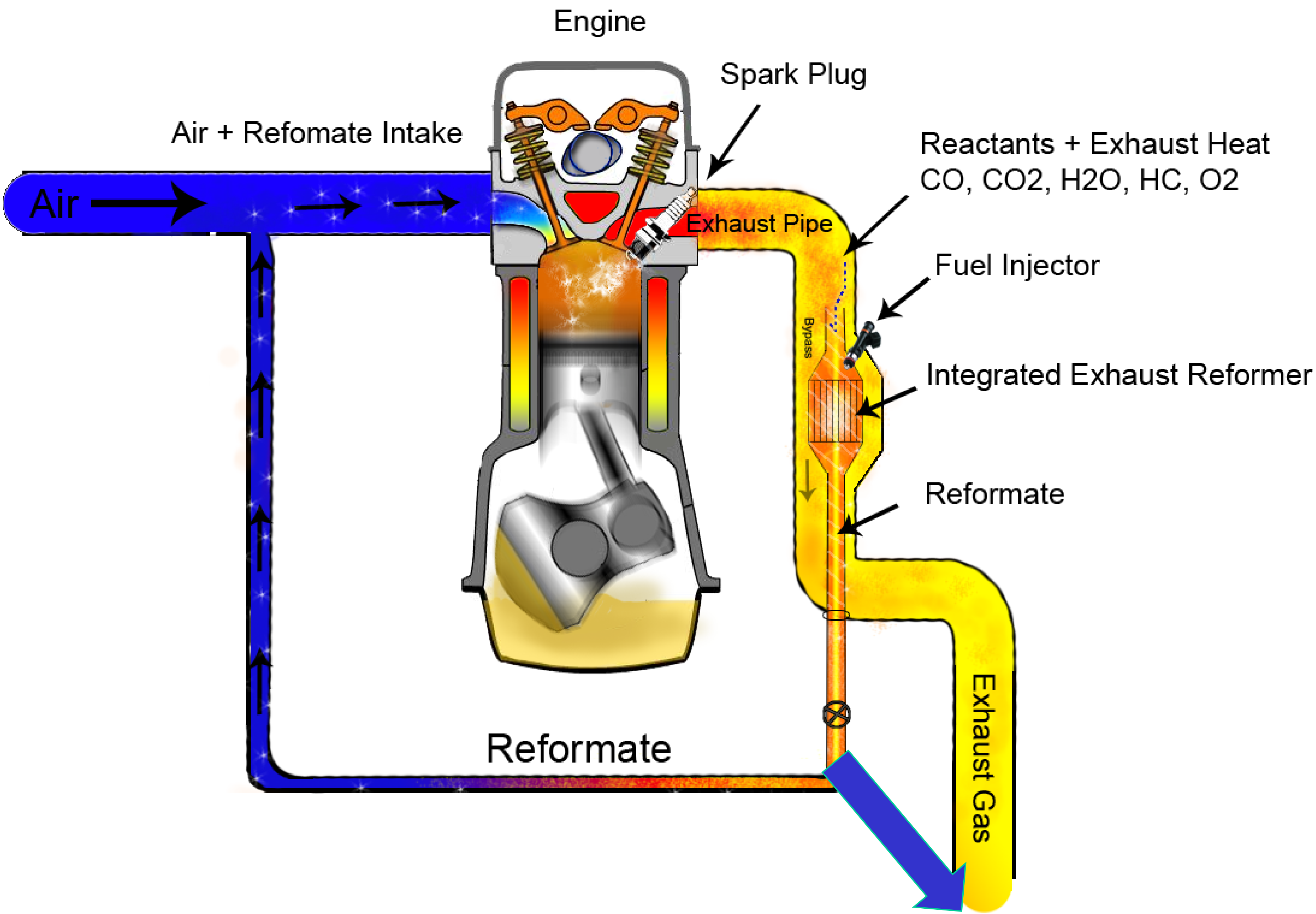
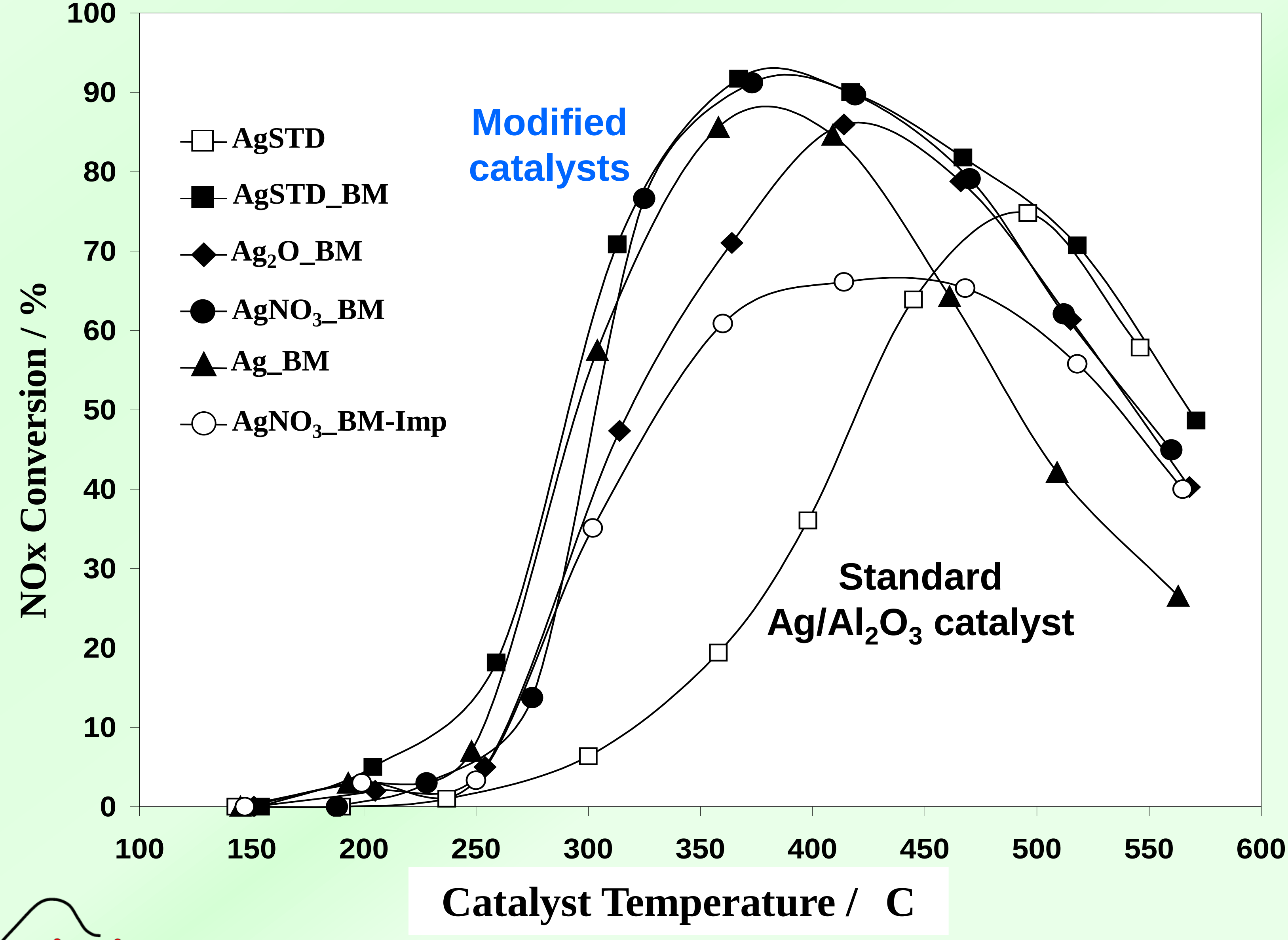


Leung et al, Energy and Environ. Sci., 3 (2010) 780-788

2. Modify the catalyst preparation



3. **investigate the reaction mechanism and use this knowledge to enhance performance.**

Are isocyanates intermediates in the HC-SCR and if so can we use them to enhance performance?

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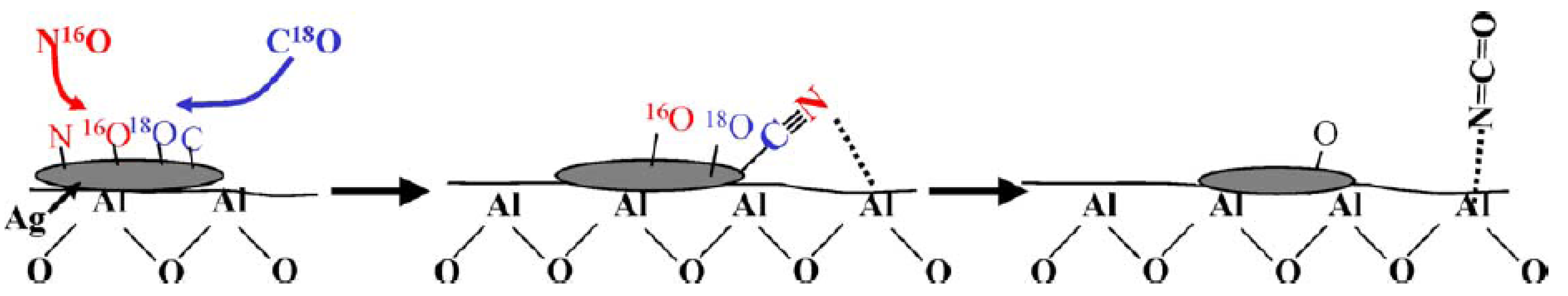
There is a route to NCO formation, and capture on the support, adjacent to silver particles



Scheme 1. Proposed formation mechanism of NCO groups in a CO + NO reaction on Ag/Al_2O_3 catalysts.

F. Thibault-Starzyk, E. Seguin, S. Thomas, M. Daturi, H. Arnolds, D.A. King, Science 324 (2009) 1048

On this basis, isocyanate may be formed on the support.

But can we determine if isocyanate is important or not in HC-SCR?

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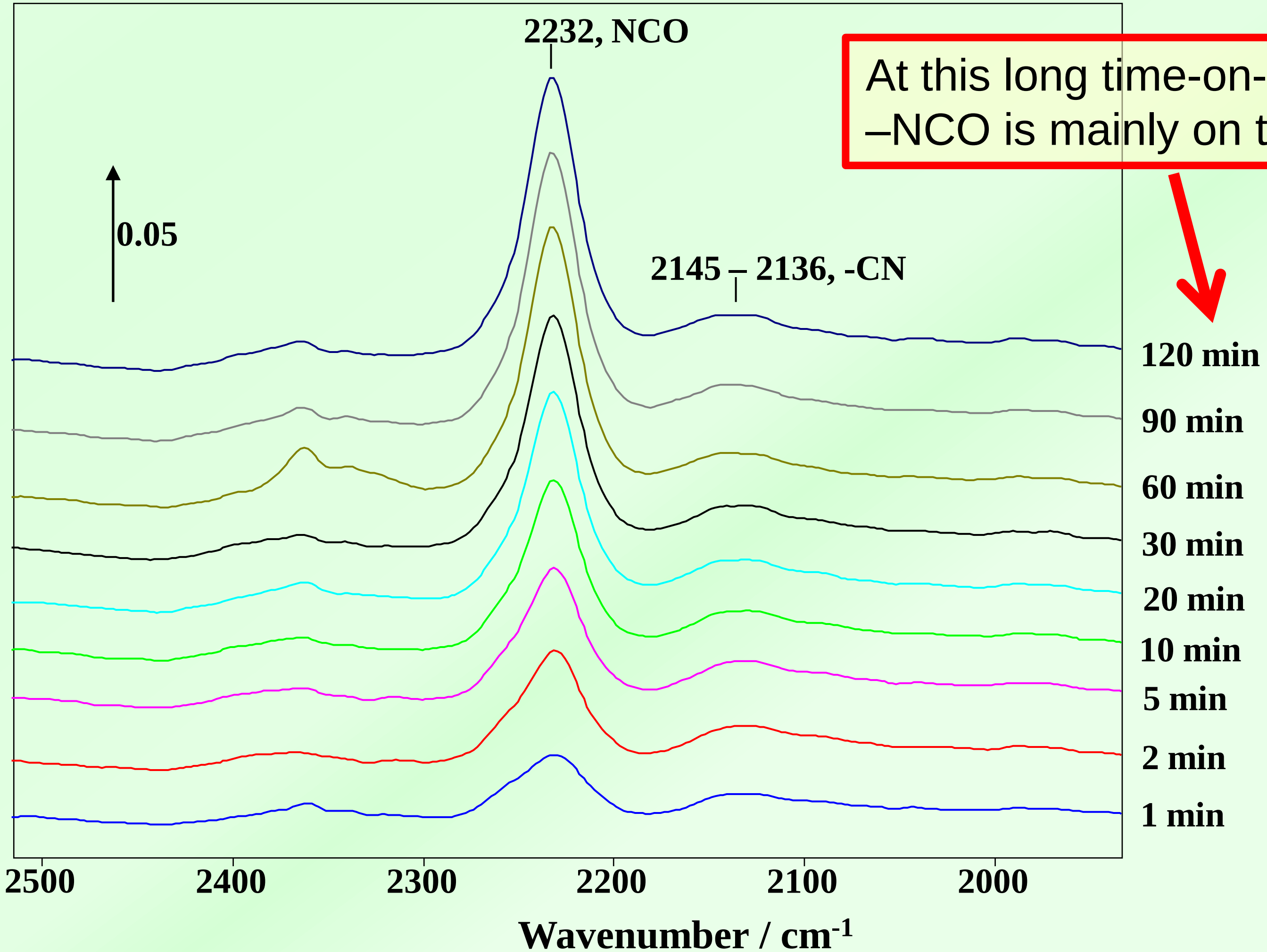
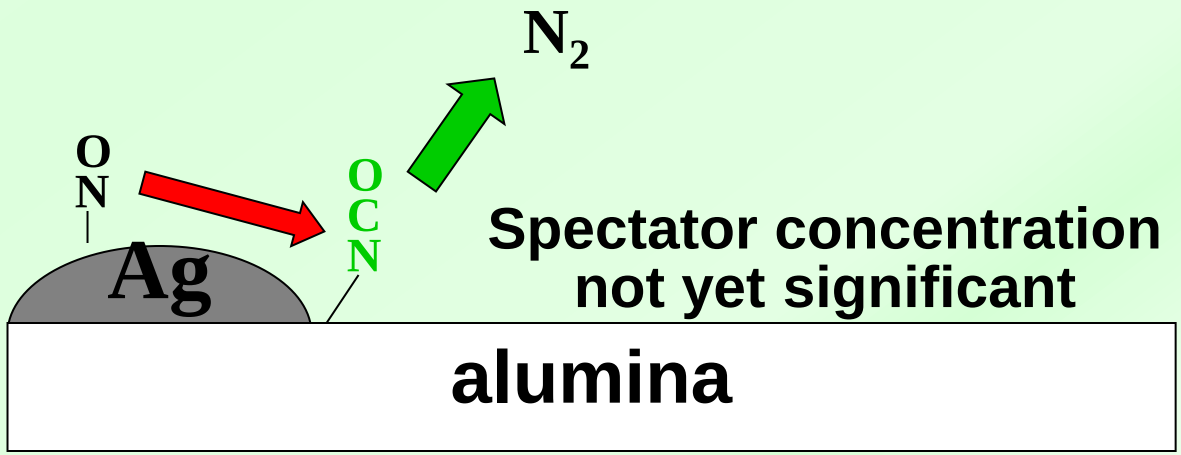
Evolution of –NCO band during reaction at 350 ºC

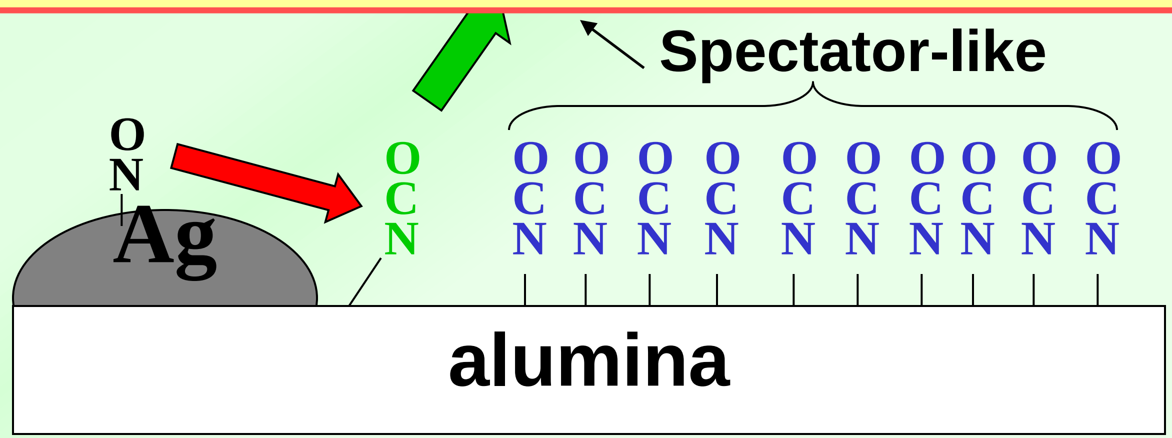


At this long time-on-stream the –NCO is mainly on the support

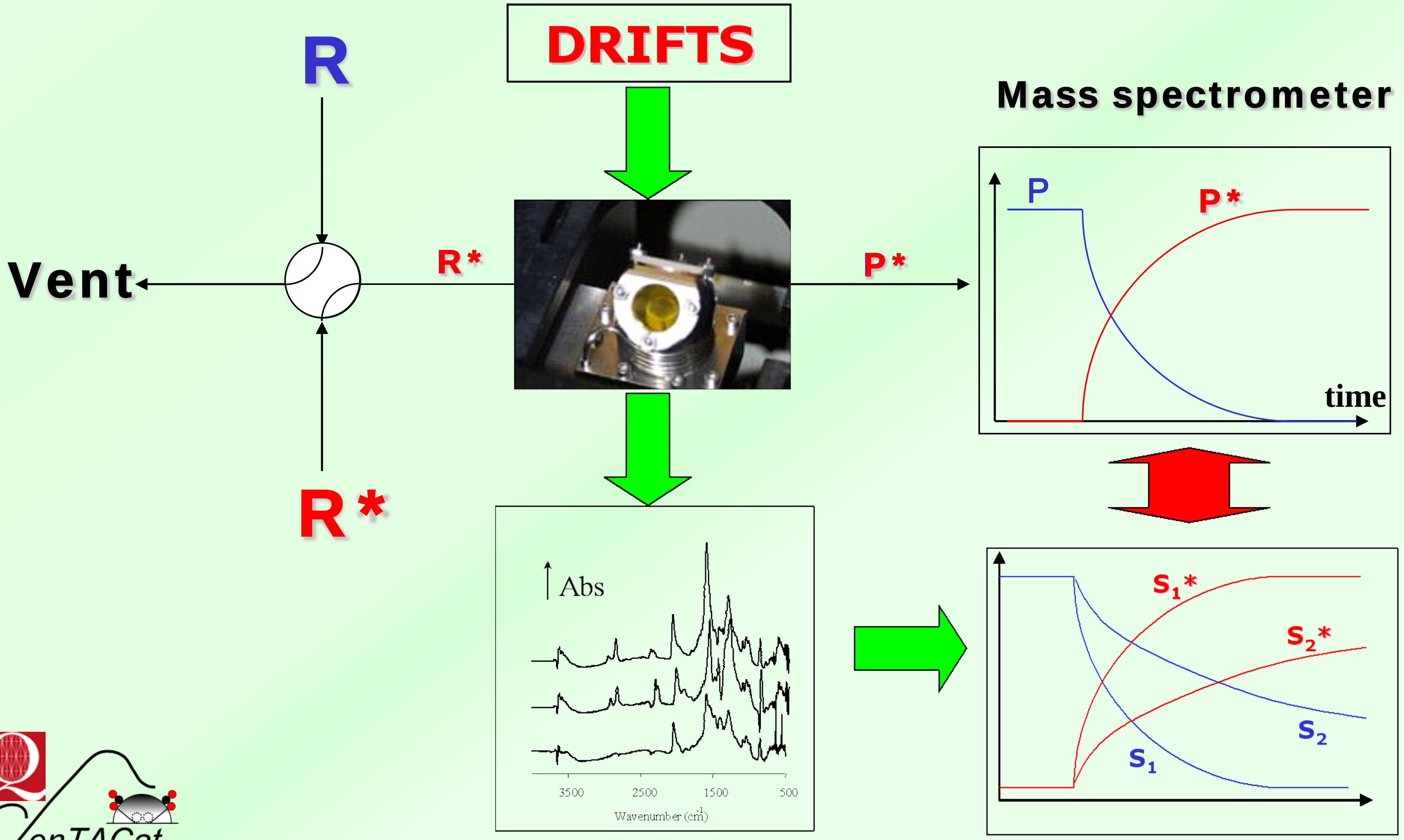
(A) at very short time on stream



Reactive **–NCO** and unreactive **–NCO** have very similar infrared signals so cannot be differentiated!



SSITKA:
Steady State Isotopic Transient Kinetic Analysis



Short time-on-stream (STOS-SSITKA) experiment

Spectator NCO species adsorb on alumina and can swamp the DRIFTS signals.

We have developed the STOS-SSITKA technique to identify reactive intermediates in the presence of a large excess of similar spectator species.

Ar $\longrightarrow$ **^{15}NO-SCR** $\xrightarrow{\text{1 min}}$ **^{14}NO-SCR** $\xrightarrow{\text{5 min}}$

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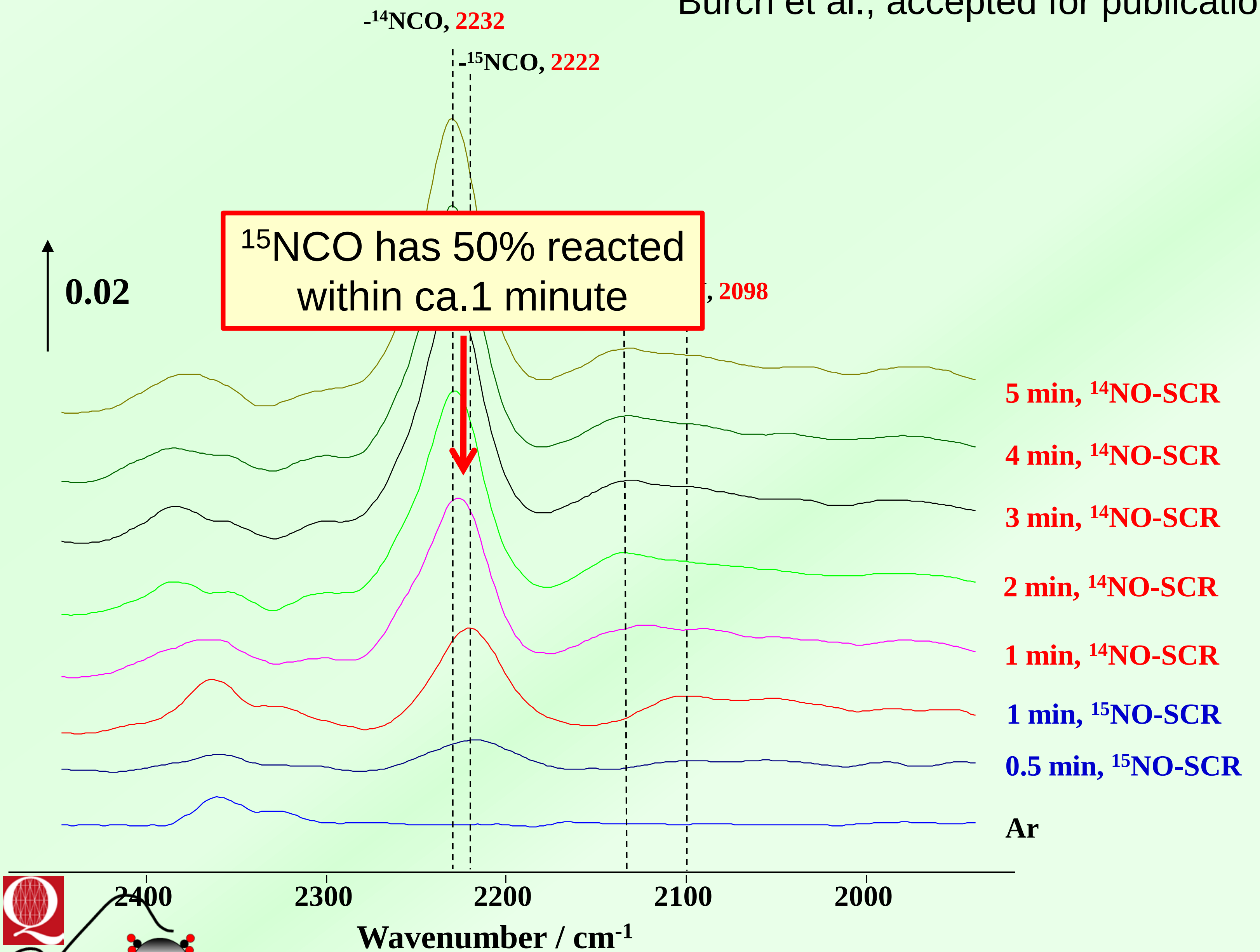
STOS-SSITKA experiment on fresh catalyst at 350 C

Burch et al., accepted for publication in J. Catal.



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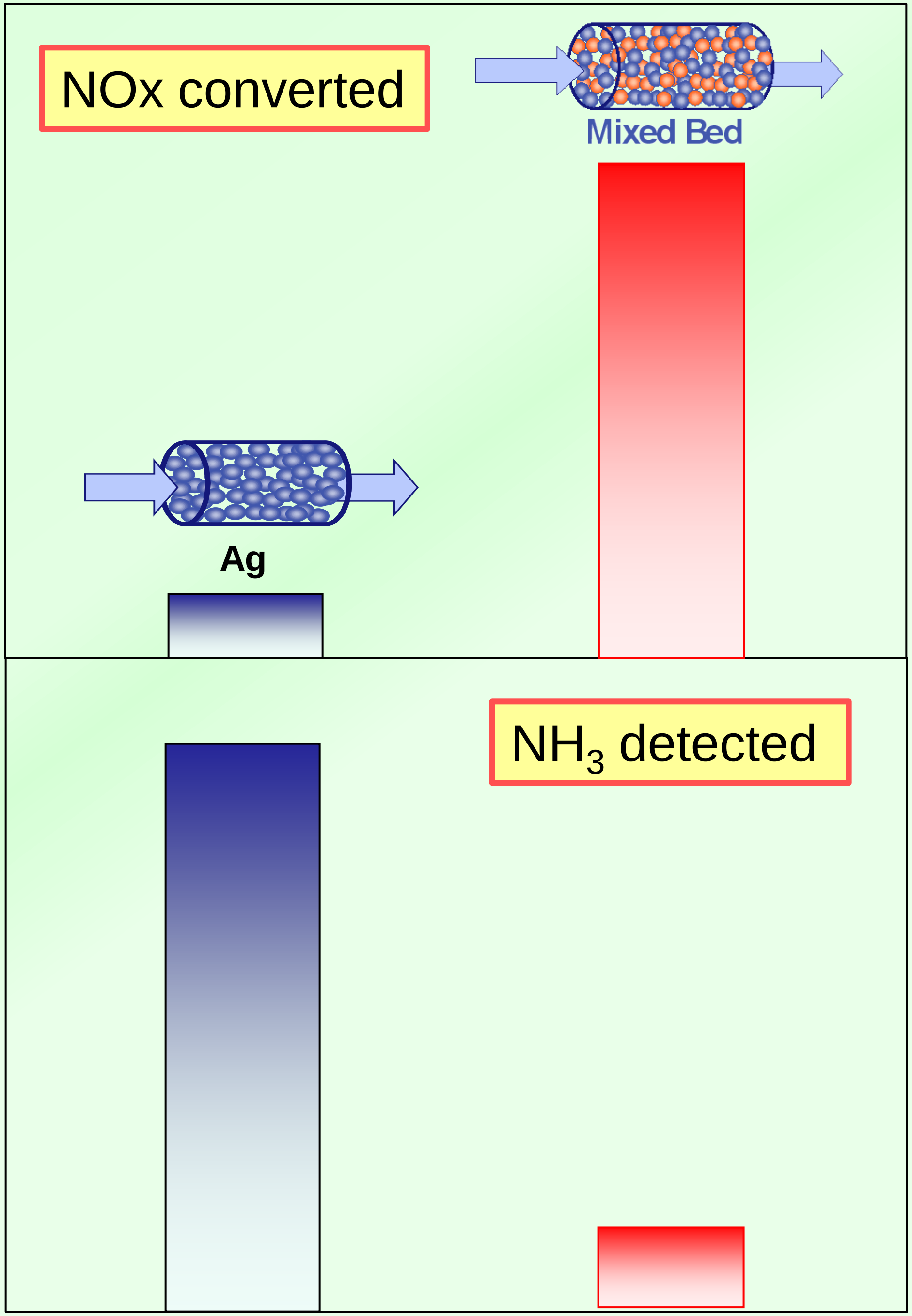
Since there are reactive isocyanate species, which are easily hydrolysed to ammonia, can we improve NOx reduction through the NH_3 - SCR reaction?

Mixed bed comprising Ag/alumina and an NH_3 SCR catalyst:
NOx conversion and NH_3 emissions

Much higher total NOx conversion and much less NH_3 seen in the outlet from the mixed bed catalyst.



Conclusions:

sensitivity to sulfur

* modification of the Ag/Al_2O_3 has provided limited benefit
* a sulfur trap designed to match the conditions in the exhaust could provide a solution.

limited low temperature activity;

* more active reductants have a significant benefit;
* modification of the catalyst preparation can increase the low temperature activity;
* based on the identification of isocyanate as a possible reaction intermediate, the use of dual bed catalysts can significantly improve de-NOx performance.

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Acknowledgements

Professor Chris Hardacre, Professor Peijun Hu,
Dr. Frederic Meunier, Dr. John Breen, Dr. Chris Hill,
Dr. Sarayute Chansai, Dr. Cyrille Rioche,
Dr. Danielle Tibiletti

Johnson Matthey
General Electric
Engineering and Physical Science Research Council (U.K.)

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