

## Modeling Light-off Profiles in Packed Bed Reactors (PBR)

Light-off profiles show reactor conversion as a function of temperature. They are quick and easy to generate, and they allow for catalyst activity to be qualitatively compared via the light-off temperature,  $T_{50}$ , at which 50% conversion,  $X$ , is achieved. In principle, very precise kinetic parameters can be obtained in a single experiment from a non-isothermal light-off profile. Non-isothermal data would be a more rigorous way to obtain  $E_A$ , because rate data from 0-100%  $X$  would be used in calculations. Changes in activity are clearly seen in non-isothermal data that are suppressed from linearization. Analysis of the rate law from a light-off profile could yield insight into the reaction mechanism under particular reaction conditions. This would allow for much quicker kinetic characterization of heterogeneous catalysts.

### Theory

Starting with the PBR design equation,  $W = C_{i,in} v_{in} \int_0^X \frac{dX}{-r_i}$

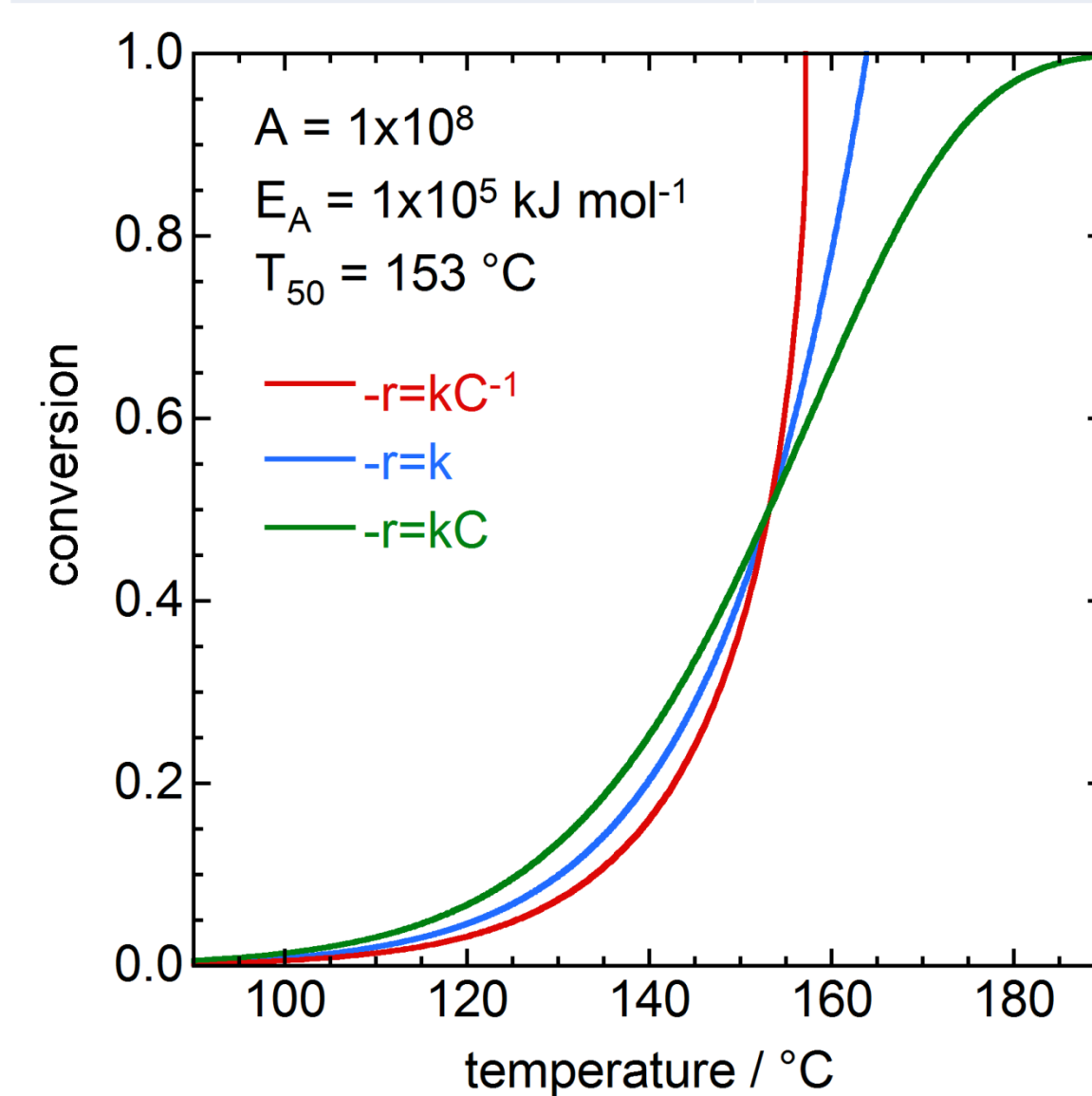
substitute a rate of reaction for  $-r_i$ , integrate, substitute the Arrhenius Equation for  $k$ , and solve for  $X$ .

Residence time,  $\tau = W / v_{in}$

Initial total volumetric flow rate  $v_{in}(T) = v_{in,ref}(T / T_{ref})$

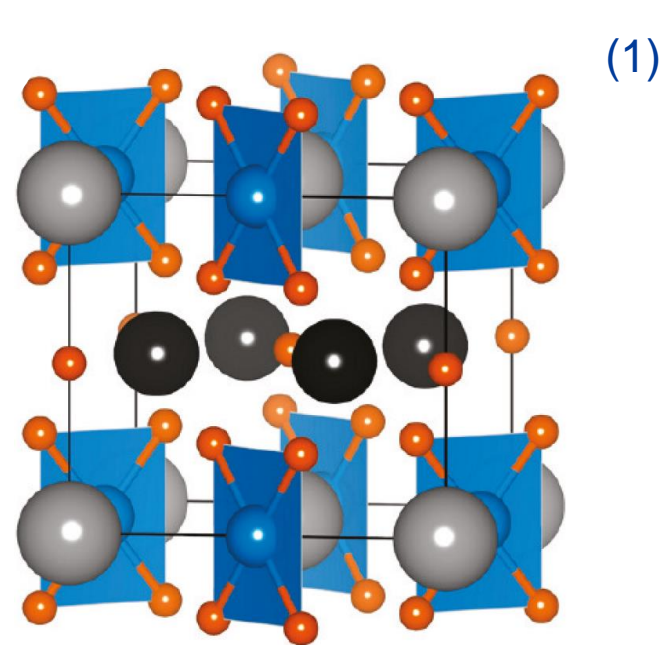
Initial concentration of species  $i$ ,  $C_{i,in}(T) = C_{i,in,ref}(T_{ref} / T)$

$-r_i$ mol g <sub>catalyst</sub> <sup>-1</sup> s <sup>-1</sup>	$X =$
$k_{obs} C_i^{-1}$	$1 - \sqrt{1 - \frac{2\tau_{ref} A}{C_{i,in,ref}^2 T_{ref}} \exp\left(-\frac{E_A}{RT}\right)}$
$k_{obs} C_i^0$	$\frac{\tau_{ref} A}{C_{i,in,ref}} \exp\left(-\frac{E_A}{RT}\right)$
$k_{obs} C_i^1$	$1 - \exp\left(-\frac{\tau_{ref} T_{ref} A}{T} \exp\left(-\frac{E_A}{RT}\right)\right)$

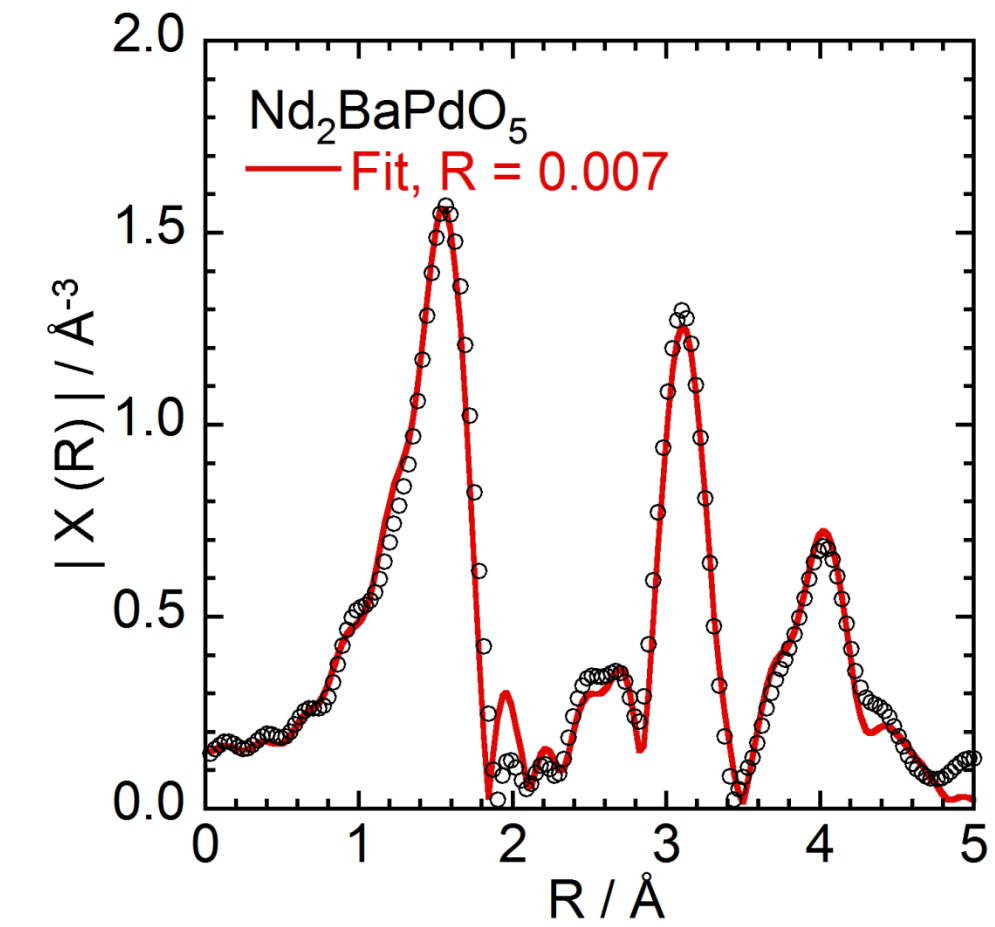
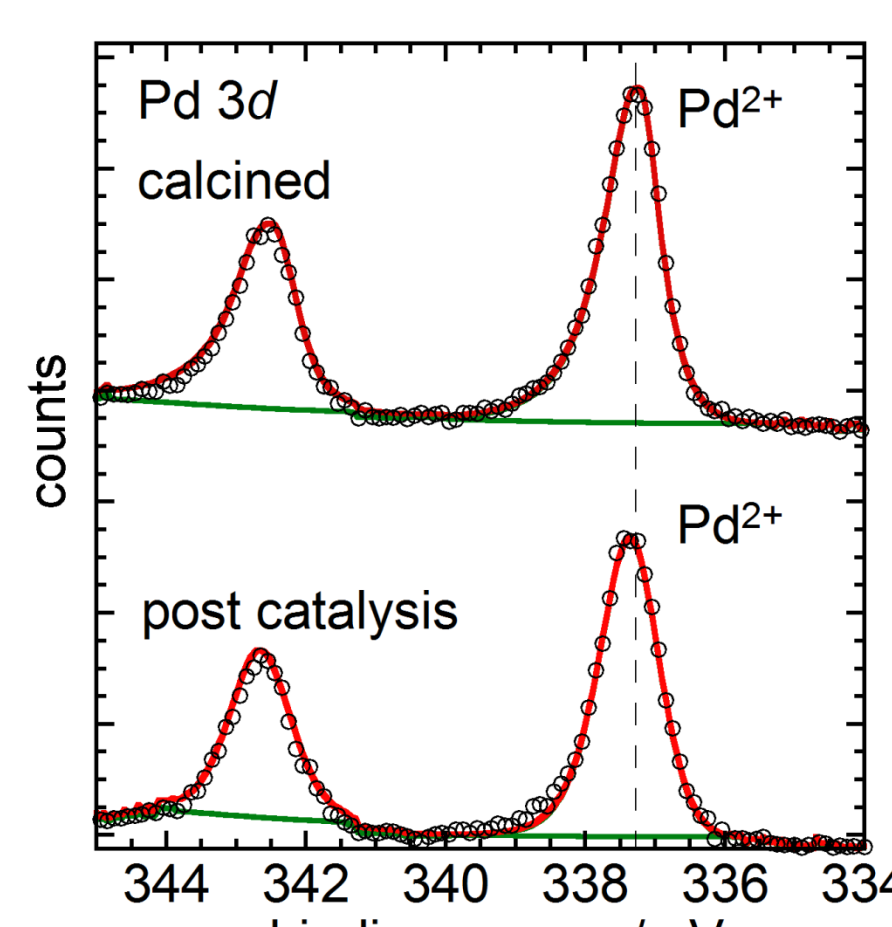


Simulated light-off profiles for inverse, zeroth, and first-order rate laws aligned to an identical  $T_{50}$ . Each simulated light-off profile has a unique  $\tau$  in order for the light-off profiles to align.

### A Stable Catalyst



$\text{Ln}_2\text{BaPdO}_5$   
low surface area  
(1 m<sup>2</sup>g<sup>-1</sup>)



X-ray absorption spectroscopy  
Fully-ordered crystal structure

- CO oxidation
- CO-lean (50 mL min<sup>-1</sup> =  $v_{in,ref}$ , 1000 ppm CO, 10% O<sub>2</sub>, Ar)
- CO-rich (50 mL min<sup>-1</sup> =  $v_{in,ref}$ , 4000 ppm CO, 1000 ppm O<sub>2</sub>, Ar)

## Simulating Light-off Profiles

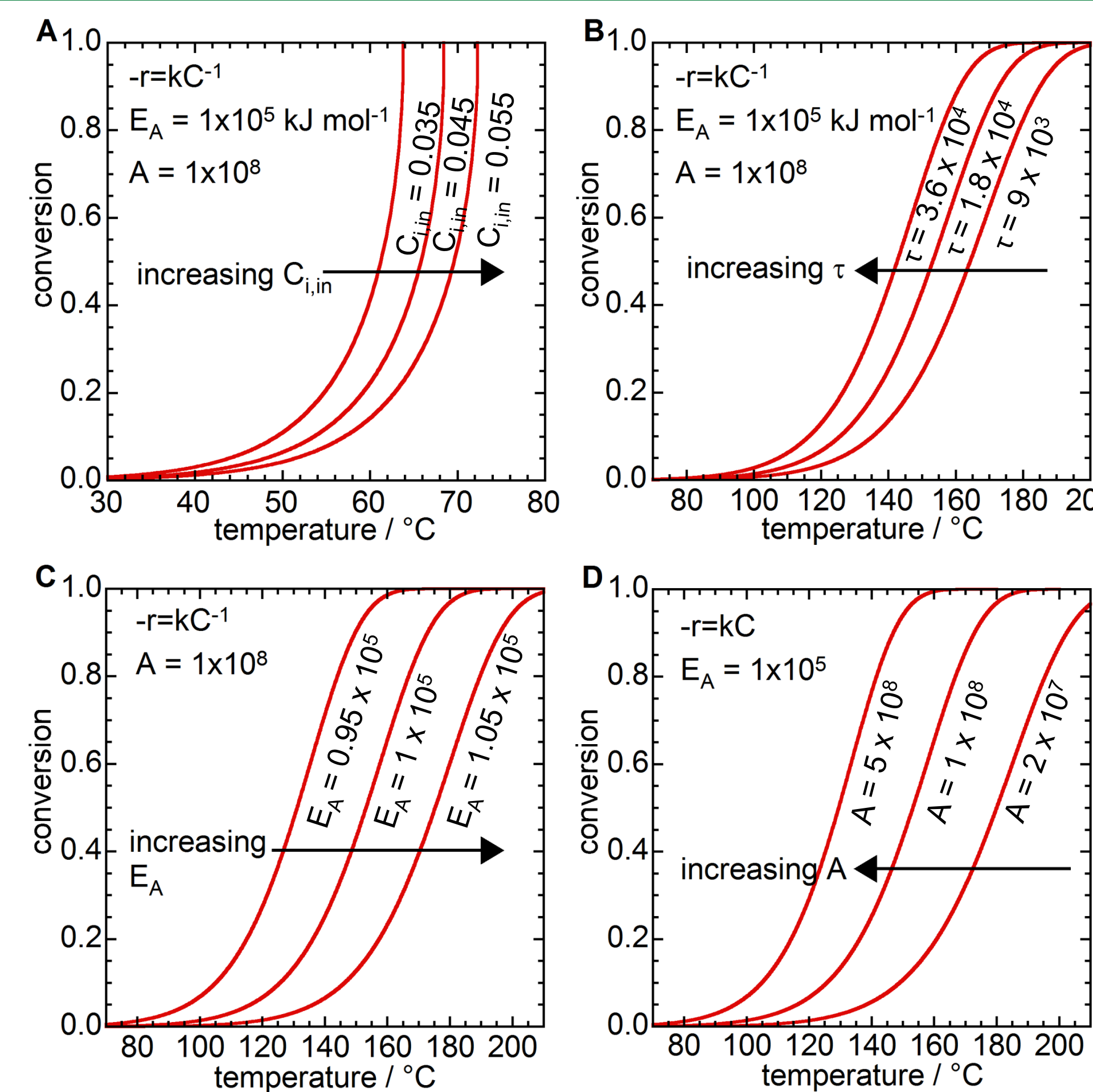
Lightoff position ( $T_{50}$ ) is not just an indication of activity.

(A) Increasing  $C_{i,in}$

(B) Increasing  $\tau$  (increasing  $W$  or decreasing  $v_{in}$ )

(C) Increasing activation energy

(D) Increasing pre-exponential factor



## Simulating Mass Transfer Effects

The observed rate of reaction can be affected by mass transfer.

**Internal Mass Transfer (IMT):** Diffusion from the catalyst surface to the interior of the pores.

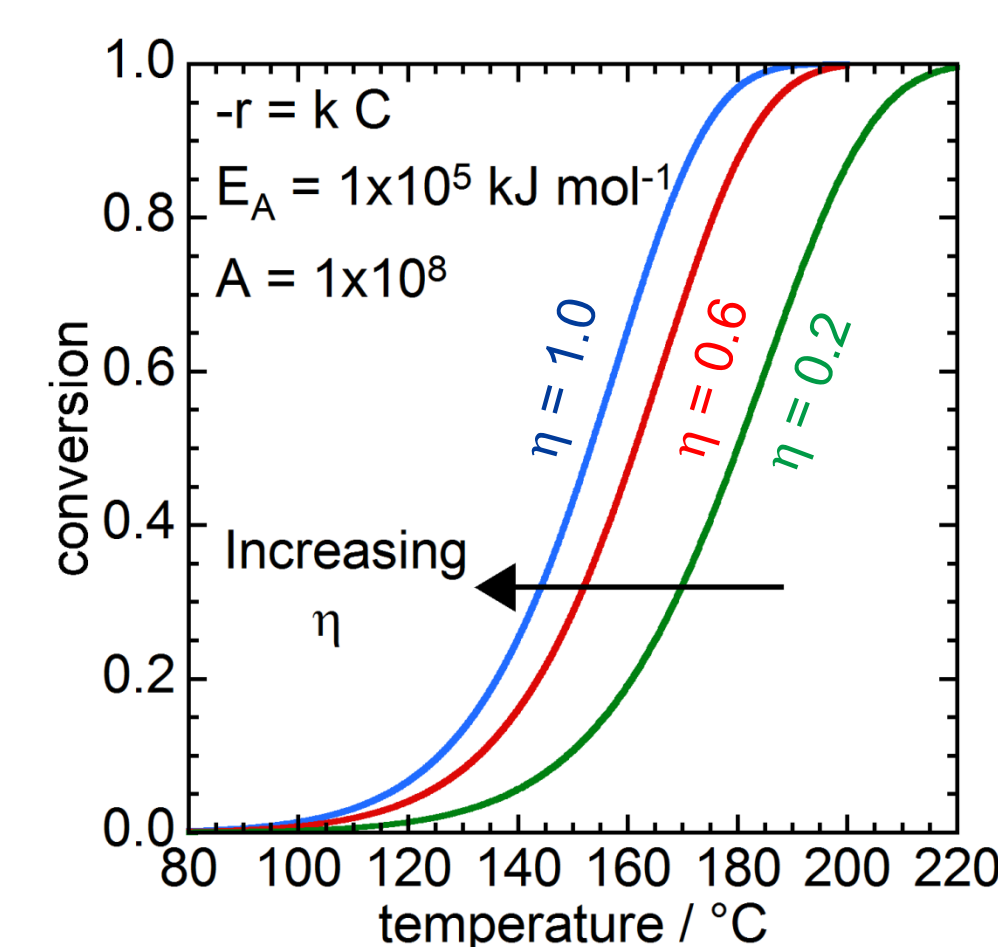
The rate can be rewritten in terms of the internal effectiveness factor,  $\eta$ .  $\eta = \text{actual rate} / \text{theoretical rate if the entire surface of the catalyst was at concentration, } C_s$ .  $-r_i = \eta k C_s^n$

**External Mass Transfer (EMT):** Diffusion from the bulk gas phase to the catalyst surface.

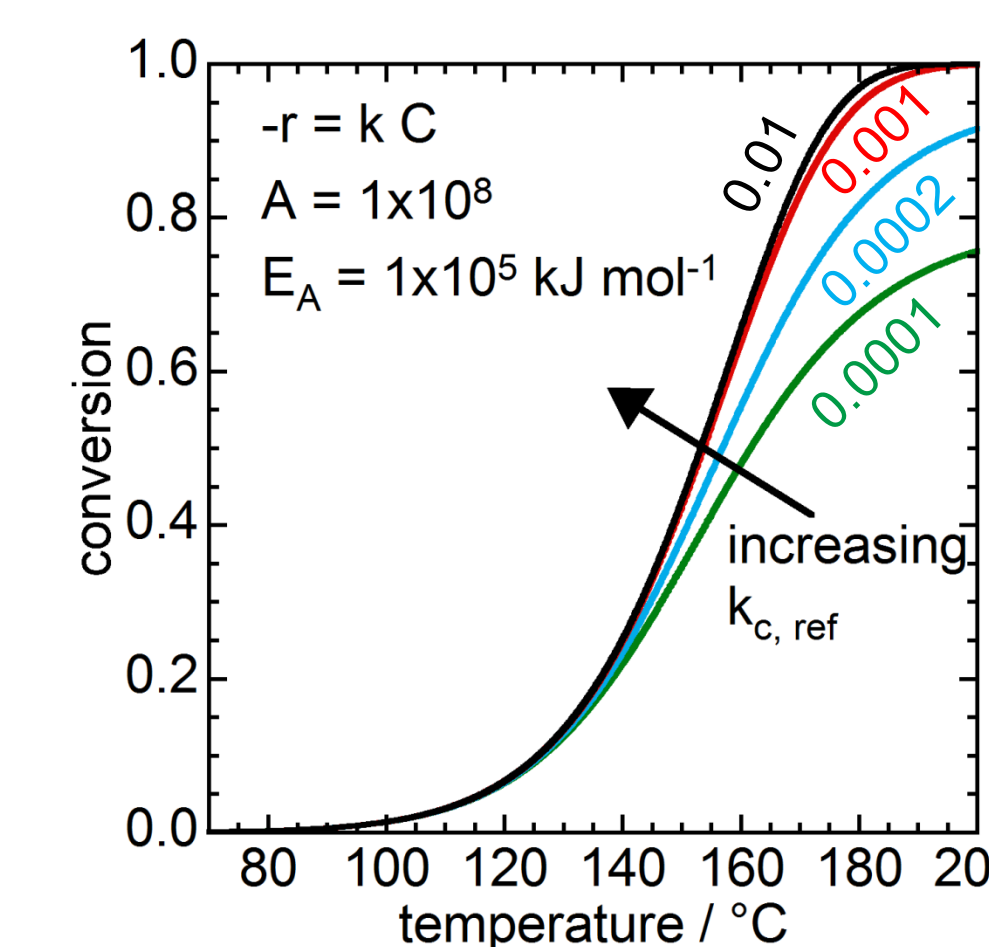
Rate of external mass transfer,  $-r_{ext} = k_{c,ref} L (T T_{ref}^{-1})^{0.79} (C_{bulk} - C_s)$

Mass transfer coefficient in a PBR,  $k_c = 1.17 Re^{-0.42} Sc^{-2/3} v_0$  (2)

Light-off equations in the presence of mass transfer	
$-r_i$ mol g <sub>catalyst</sub> <sup>-1</sup> s <sup>-1</sup>	$X =$
$k_{obs} C_i^{-1}$	N/A
$k_{obs} C_i^0$	$\frac{\eta \tau_{ref} A}{C_{i,in,ref}} \exp\left(-\frac{E_A}{RT}\right)$
$k_{obs} C_i^1$	$1 - \exp\left(-\frac{k_c L \eta \tau_{ref} T_{ref} T^{-1} A \exp\left(-\frac{E_A}{RT}\right)}{A \exp\left(-\frac{E_A}{RT}\right) + k_c L}\right)$

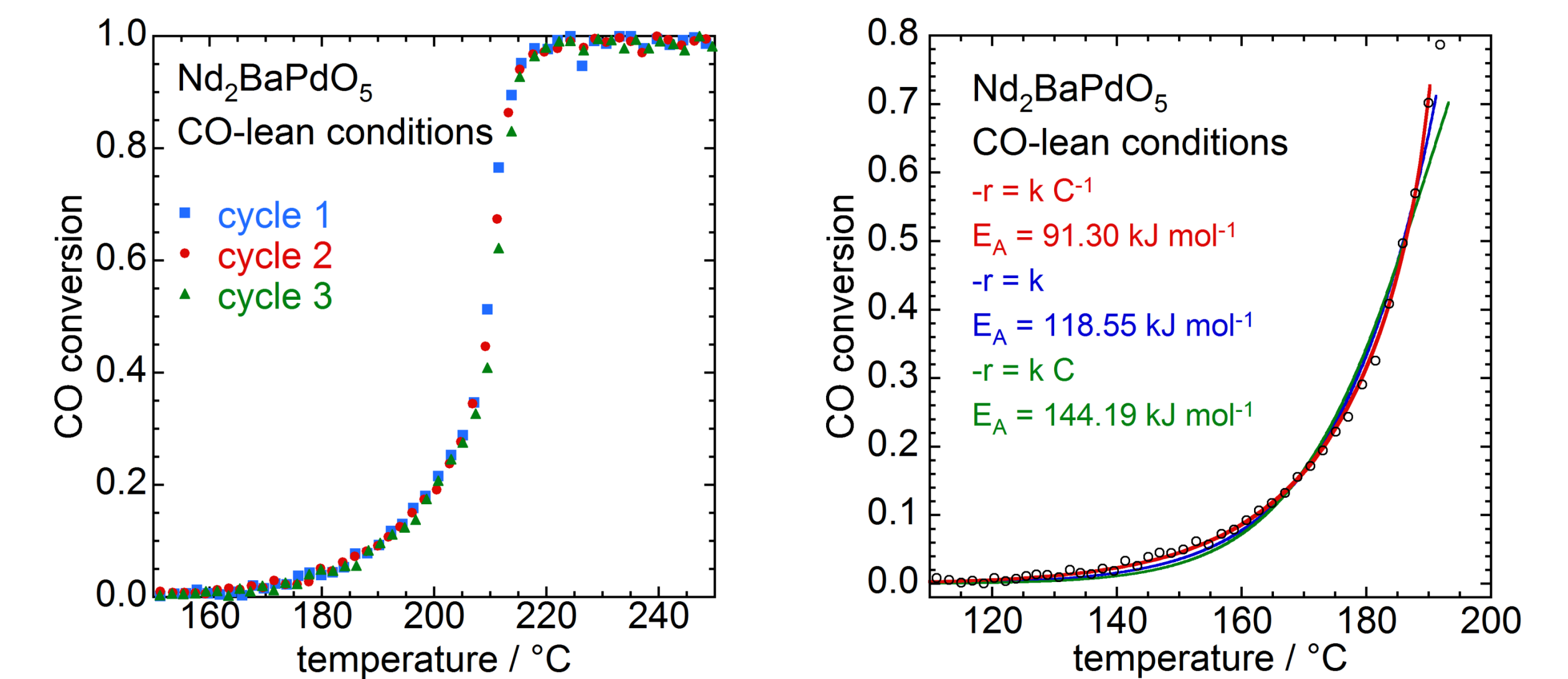


Slow IMT increases  $T_{50}$  and increases the rate at which activity decreases at high  $X$ .



Slow EMT increases  $T_{50}$  and decreases the theoretical maximum conversion.

## Experimental Results

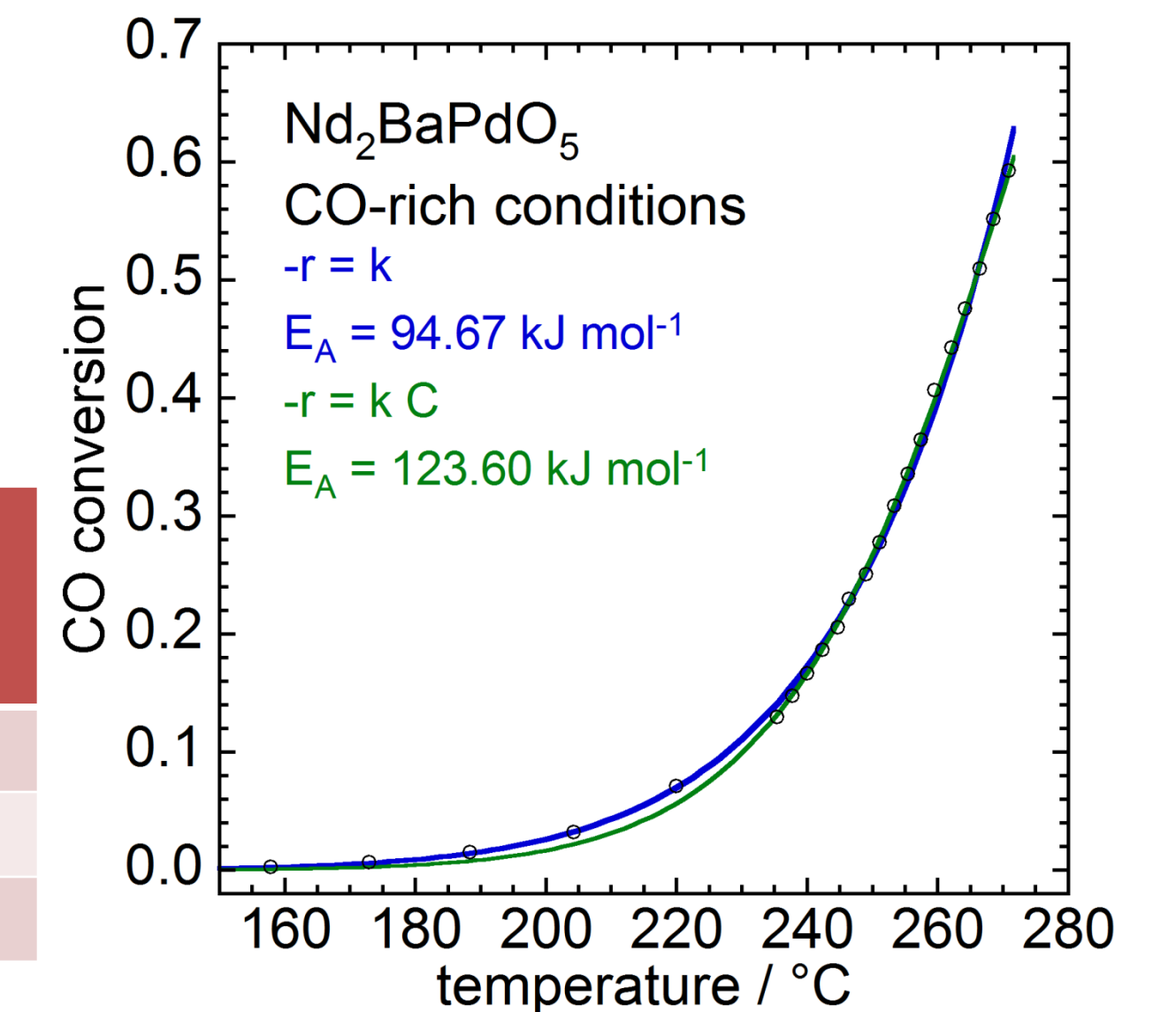


Reproducible light-off profiles were produced after pre-treating the catalyst under reaction conditions for 1 h at 300°C. The data were truncated at  $X = 70\%$  and fit. The  $\text{Ln}_2\text{BaPdO}_5$  catalysts obey an inverse-first-order reaction rate under CO-lean conditions

$E_A$ (kJ mol <sup>-1</sup> ) for CO oxidation under CO-lean conditions by $\text{Nd}_2\text{BaPdO}_5$ and $\text{Dy}_2\text{BaPdO}_5$		
Catalyst	Light-off Fit	Arrhenius
$\text{Nd}_2\text{BaPdO}_5$	91.30 ± 0.09	96 ± 5
$\text{Dy}_2\text{BaPdO}_5$	124.47 ± 0.10	125 ± 7

Under CO-rich conditions the reaction order changes to a pseudo-zero-order rate law. The data were truncated at  $X = 60\%$  and the light-off equations were fit to the data.

$E_A$ (kJ mol <sup>-1</sup> ) for CO oxidation under CO-rich conditions by $\text{Nd}_2\text{BaPdO}_5$ and $\text{Dy}_2\text{BaPdO}_5$		
Catalyst	Light-off fit	Arrhenius
$\text{Nd}_2\text{BaPdO}_5$	94.67 ± 0.19	90 ± 7
$\text{Dy}_2\text{BaPdO}_5$	94.12 ± 0.17	97 ± 6



## Conclusions

The activation energies obtained from our non-isothermal kinetic analysis are in agreement with the values obtained from the traditional Arrhenius analysis. Inspection of non-isothermal data can yield kinetic parameters and information about the reaction order. Under CO-lean and CO-stoichiometric conditions, the catalysts followed an inverse-first order rate law, while under CO-rich conditions the catalyst followed a zeroth-order rate law. We are able to observe changes in activity during reaction that would not be observed from isothermal experiments.

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## References

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Stanford Synchrotron Radiation Laboratory  
Stanford Linear Accelerator Center

