

## Kinetics and Reactor Design (Graduate) Homework Problem Nitrogen Oxide Catalytic Reduction

Lean-burn combustion (burning fuel with an excess of air) is employed in many internal combustion engines to increase efficiency during normal driving (i.e. steady pace, not accelerating) and can reduce the emission of hydrocarbons (not CO or CO<sub>2</sub>). Unfortunately, lean-burn combustion also increases the production of harmful nitrogen oxide (primarily NO & NO<sub>2</sub>, i.e. NO<sub>x</sub>) species. NO<sub>x</sub> species cause a wide variety of health and environmental issues; they contribute to the formation of ground-level ozone, smog, and acid rain, but they can also react to form nitrate particles or acid aerosols, all of which can trigger serious respiratory problems.

In response, nitrogen oxide selective catalytic reduction (NO<sub>x</sub> SCR) has been developed as an exhaust gas treatment process to convert NO<sub>x</sub> species, formed during lean-burn combustion, to more benign molecules, N<sub>2</sub> and H<sub>2</sub>O. Understanding adsorption/desorption properties of NO is key to developing more active catalysts for this reaction.

In addition, various policies have been considered or implemented to incentivize emission reductions, but these are complicated issues. Considering industrial emissions, “cap and trade” systems have been developed which set an upper limit on the allowable emissions from a particular business but allows further capacity to be purchased from other businesses who have not used their full allowance. While these policies ostensibly encourage emissions reduction, they can also result in “emission hotspots” that disproportionately affect low-income or minority communities or increase production costs that eventually fall on the consumer, again impacting low-income individuals.

### References

1. Alkemade, U. G.; Schumann, B., “Engines and exhaust after treatment systems for future automotive applications.”
2. *Solid State Ionics*, 2006, 177 (26), 2291-2296. <https://doi.org/10.1016/j.ssi.2006.05.051>  
Farber, Daniel A. “Pollution Markets and Social Equity: Analyzing the Fairness of Cap and Trade.” *Ecology Law Quarterly*, 2012, 39(1), 1–56. <http://www.jstor.org/stable/24113488>
3. United States Environmental Protection Agency: Basic Information about NO<sub>2</sub> (<https://www.epa.gov/no2-pollution/basic-information-about-no2>)

### Questions

- a) If the sticking probability of NO on Cu is given by  $S(\theta) = 0.08 \times (1 - \theta)$ , is this likely a dissociative or non-dissociative adsorption process? Defend your answer.
- b) Given your answer to part a, write the general form of the Langmuir isotherm for this adsorption process.
- c) What is the NO molecular flux at a temperature of 473 K and a pressure of P torr. (Leave answer in terms of P with final flux units of molecules/(s\*cm<sup>2</sup>)).
- d) What is the rate of adsorption for NO on a Cu surface? (Express in terms of  $\theta$  and P.)

- e) Experiments suggest that desorption of NO from a Cu surface is described by the following empirical rate:

$$r_{des} = 10^{10} s^{-1} \times \theta \times \exp\left(\frac{-E_a}{RT}\right) \times N_s \quad \text{where } E_a = 50 \text{ kJ/mol. This simplifies to:}$$
$$r_{des} \approx 3 \times 10^{19} \times \theta \text{ molecules/s} \times \text{cm}^2$$

Solve for the actual adsorption isotherm for NO on Cu. What is the value of  $K_{NO}$  based on this result?

- f) Please consider the following questions and share your thoughts in few sentences or bullet points.
- i) What other technologies are aimed directly at reducing emissions? Are these technologies equally beneficial and accessible to individuals that are impacted by emissions?
  - ii) Are there ways that we could design policies to encourage or require reduction of emissions that are more equitably implemented?