**Modeling**

In this section, we look at the desorption of CO from the surface of a Pd(111) lattice. We want to study the kinetics of this reaction. It’s shown in [CITE] that CO can adsorb onto different sites (a – top, bridge, and hollow) depending on the temperature and pressure of the system. Since our experiments are carried out at temperatures , we are dealing with a case where adsorption occurs only onto bridge and hollow sites [CITE].

Here, we will preliminary consider only a simplified modeling of the system, in which we do not care about the adsorption site, rather, we consider the total amount of CO adsorption on the surface. The modeling and full analysis of the system, in which we account for the different sites, as well as for both adsorption and desorption and other reaction details, is left for an upcoming paper.

The chemical reaction can be written as

Eq. 1

where COX is CO adsorbed onto the Pd surface, and k is the desorption rate. Our collected data is a time series of the coverage of CO onto Pd(111) and our objective is to find the kinetic parameter k. Let us denote the coverage of CO onto Pd(111) at time with and let. Then, the rate reaction can be described with a linear differential equation

Eq. 2

which can be analytically solved by simple separation of variables, and yields the following equation:

Eq. 3

By taking the natural log on each side, we can rearrange the equation to fit a simple linear regression model [1]

Eq. 4

given the set of points . Fitting this regression line amounts to applying ordinary least squares [2] to get the best fit line.

The desorption rate constant k was estimated as described above for four different datasets pertaining to temperatures of The data was fitted using the estimated parameter k into equation 3, assuming we have the starting data point .

The fittings for each dataset are shown in Figure X.

Chart, scatter chart

Description automatically generated

Figure X. Coverage fitting for temperatures at

The scattered plots represent the experimental data. The line plots represent the fittings.

The estimated desorption constants k for the temperatures were respectively. Using these estimates, an Arrhenius plot (see Figure Y) was used to obtain the activation energy of desorption Ea, as well as the pre-exponential factor A.

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Figure Y. Arrhenius plot

The activation energy obtained is Ea = 26.48 kcal, and the pre-exponential factor A = 5.95 x 1011. What is it compared to literature value?

1. Citation for simple linear regression

Zou, Kelly H., Kemal Tuncali, and Stuart G. Silverman. "Correlation and simple linear regression." *Radiology* 227.3 (2003): 617-628.

2. Citation for OLS:

Hutcheson, Graeme D. "Ordinary least-squares regression." *L. Moutinho and GD Hutcheson, The SAGE dictionary of quantitative management research* (2011): 224-228.

In case we want to use only the three temperatures.

Chart

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k constants = {}

Ea = 25.77 kcal

A = 2.93 x 1011

Data Conversion

The resulting IRRAS data (after averaging X cycles) is a time series. A data point at a single time instant is an absorbance spectrum with a peak at a certain wavenumber. The peak is indicative of the amount of CO adsorbed onto the Pd(111) surface at that time. To learn the kinetics of the reaction, our goal is to first convert the IRRAS data to coverage of CO in time. To do this, we make use of the figure M from [CITE], which relates coverage with wavenumber. This correlation has led us to convert the data in two ways, which we describe below.

1. Coverages below 1/3.

Figure M shows that for coverages below 1/3, there is not much change in frequency. In that case, a reliable approach is to obtain the coverage through Beer Lambert’s law [CITE], which states:

Eq. 5

where is the area under the curve of a spectrum taken at time , is the coverage of CO at time , and is the absorptivity constant. The area under the curve was obtained in Origin using a baseline approach. The baseline was centered at a level which averages the noise to 0.

Once we have the area with time, we use the area at a given wavenumber, and the coverage at that wavenumber (from [CITE]) to find the absorptivity . Then, all the coverages below 1/3 are found using the obtained area points and the absorptivity in Eq.5.

1. Coverages above 1/3.

Figure M shows that the frequency for coverages above 1/3 changes rapidly. In this case, we cannot use an absorptivity constant. Instead, we fit a function relating coverage with wavenumber (using the data from Fig. M). We evaluated the fitted function at the collected wavenumbers in our data and obtained coverage data with time. The fitted function is

Eq. 6

where is wavenumber. Using these two approaches, we obtain a time-series data of coverage of CO onto Pd(111), which helps us further in understanding and modeling the kinetics of the reaction.