10240 Design-Build 2: Rational catalyst design for General Engineering

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Contents

1 Used equipment

- 10 mL graduated cylinder
- 100 mL conical flask with a connecting piece
- Rubber stopper
- Plastic tube
- Magnetic stirrer
- Tray
- 2 stands w/clamps
- Stopwatch
- 2 beakers
- 3% H_2O_2 (hydrogen peroxide)
- 0.2 M NaOH (sodium hydroxide)
- Foils: Cu, Ni, Rh, Pd
- Caliper

2 H_2O_2 decomposition

During the H_2O_2 decomposition experiment the volume of produced oxygen was tested over a period of time. The experiment was performed using 4 different catalysts: Rhodium (Rh), Copper (Cu), Palladium (Pd) and Nickel (Ni). The oxygen evolution rates for all these metals can be determined by the following plots:

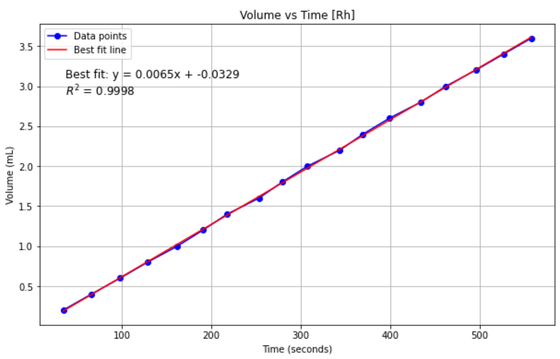

Figure 1: Oxygen produced over time (Rh)

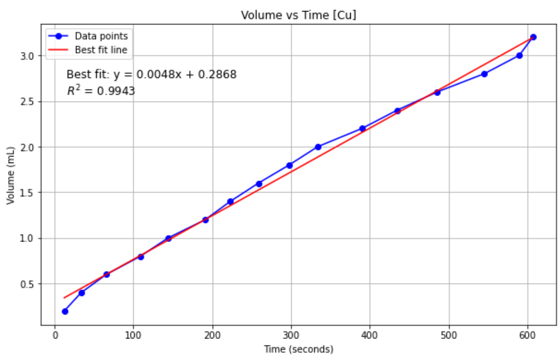

Figure 2: Oxygen produced over time (Cu)

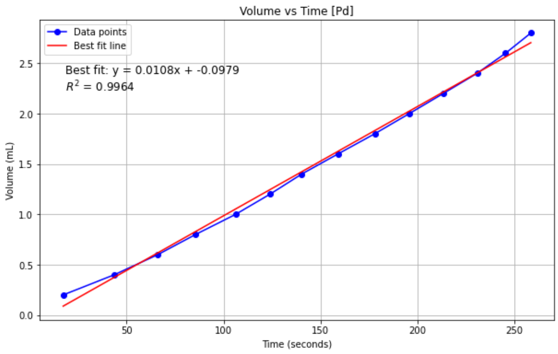

Figure 3: Oxygen produced over time (Pd)

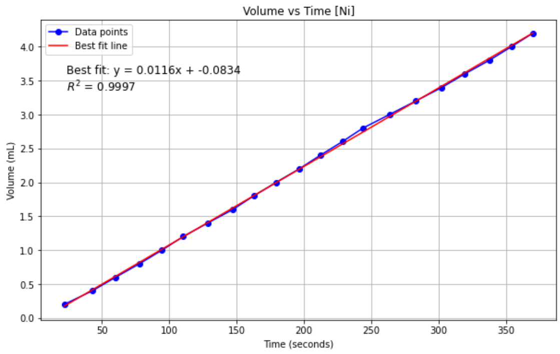

Figure 4: Oxygen produced over time (Ni)

To calculate catalytic activity we found the "slope", the oxygen evolution rate, which has units of ml/s, using linear regression. As oxygen is the gas we can easily convert ml to moles by using the following relationship: $22.4mol = 1L$. In this way, we can obtain mol/s. And the only thing missing is the area of the catalyst, which we found by simple measurements.

$$Activity = \frac{volume}{time \cdot area \cdot 22.4 \cdot 10^3}$$

The plot below summarizes all the plots above:

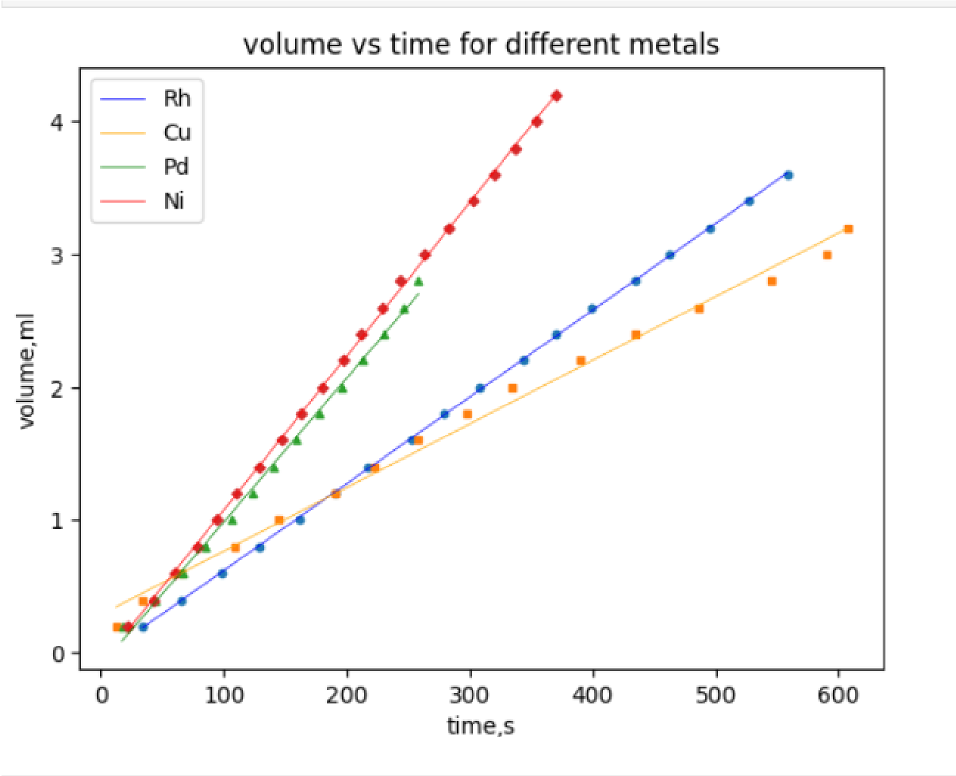

Figure 5: Oxygen evolution rate

We can see that Ni and Pd both have higher oxygen evolution rates. However, concluding their height reactivity would be a big mistake as we didn't account for the area of a catalyst. The table below summarizes all calculations, as well as, the catalytic activity that accounts for the area. The OH binding energies were calculated from the data provided in the g-bar by the formula $\Delta G(\mathrm{OH}^*) = G(\mathrm{OH}^*) - G(*) - \left(G(\mathrm{H_2O}_{(l)}) - \frac{1}{2}G(\mathrm{H}_{2(g)})\right)$.

Material	OH binding energy (eV per molecule)	Specific surface area (m^2/g)	Mass (g)	Area (m^2)	Oxygen evolution rate (mL/s)	Catalytic activity ($mol/s/m^2$)
MoO_2	-0.64	0.169	0.682	0.1153	0.0575	0.0000207
MnO_2	1.90	0.887	0.132	0.1171	0.7603	0.0002899
TiO_2 (rutile)	3.60	2.321	0.527	1.2232	0.005	1.825e-07
Rh	1.40	NaN	NaN	0.0000773617	0.006533	0.00377
Cu	1.11	NaN	NaN	0.0006138	0.004791	0.000348
Pd	1.57	NaN	NaN	0.0000708036	0.01084	0.006835
Ni	0.86	NaN	NaN	0.000450	0.011589	0.001151

Table 1: Experimentally obtained catalytic properties of different materials

The plot below is the so-called "vulcano plot" and it is a good representation of Sabatier's principle.

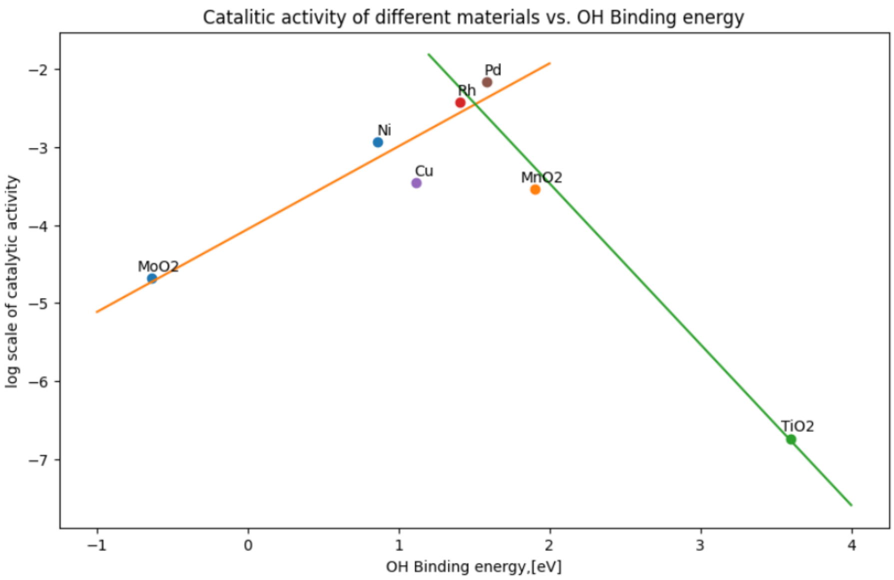

Figure 6: Vulcano plot with logarithmic scale of catalytic activity on the left axis and the corresponding OH binding energies on the right axis

The right side of the vulcano plot shows low binding energies, which means the interaction between OH and the surface of the catalyst is weak consequently the $HO - OH$ bonds are less likely to break. The left side is opposite to the right: the bonds are too strong, which hinders the adsorption process. The peak of the volcano plot shows us the best catalysts that balance these two extremes.

The time evolution might curve down toward the end, one possible reason is that the concentration of $H2O_2$ decreases, leading to a reduction in the evolution of oxygen. Another reason could be interactions of the catalyst surface with the reactants, such as surface oxidation, which can hinder the reaction flow.

As for the reasons for increased measured activity, I can think about the increased temperature of the medium during the reaction which will speed up the reaction.

3 Uncertainties

As in the lab manual, we were asked only about one uncertainty measurement, so we chose Rhodium.

The logarithmic activity can be calculated by the following formula:

$$f = log(\frac{slope}{\pi(dh + d^2/2) \cdot 22.4 \cdot 10^3}) \tag{1}$$

, where "slope" is the oxygen evolution rate, d -diameter, and h is the length of the catalyst sample.

We decided to calculate the error using the error propagation formula, which is

$$df = \sqrt{(\frac{\partial f}{\partial d} \cdot \Delta d)^2 + (\frac{\partial f}{\partial h} \cdot \Delta h)^2 + (\frac{\partial f}{\partial slope} \cdot SE)^2} = \tag{2}$$

$$\sqrt{(-\frac{(d+h)}{(d^2/2 + dh)\ln(10)} \cdot \Delta d)^2 + (-\frac{d}{(d^2/2 + dh)\ln(10)} \cdot \Delta h)^2 + (\frac{1}{slope \cdot \ln(10)} \cdot SE)^2} \tag{3}$$

, where Δh and Δd are errors of measuring device, caliper $= 1mm$ and micrometer $= 0.002mm$ respectively. SE - standard error of the slope calculated when performing linear regression model, it was automatically given by the function in Python, and equals $4.885e - 05$. The values we had:

$$h = 49 \cdot 10^{-3}$$
$$d = 500 \cdot 10^{-6}$$
$$slope = 0.006533$$
$$\Delta h = 1 \cdot 10^{-3}$$
$$\Delta d = 2 \cdot 10^{-6}$$
$$SE = 4.885e - 05$$

After substituting all values we found the uncertainty to be around 0.01. As the error is small it can't be seen on the plot represented as an error bar.

From myself, I would never believe in this uncertainty. I would at least add 10% to the existing measurement looking back at how we measured bent wire with caliper.

4 Conclusion

Returning to Figure(6), we can conclude that Rhodium and Palladium are the best catalysts.

5 Appendix