

REU 2004 Summer Program

# Catalyst Preparation

## Uptake of Gold onto Different Supports

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## Abstract

Catalysts play a key role in industry, as well as everyday life. A catalyst's main function is to increase the rate of a reaction without being consumed. Catalyst's increase productivity and efficiency, which translates into increase in profit, which is why finding more catalysts is such an important topic today. Solid catalysts are composed of metals or metal oxides that form supports onto oxides and create metal particles with high surface areas. The goal is to form small metal particles with high surface areas, since reactions take place on the surface, so the more surface area, the more the reaction can take place. A main goal of catalyst preparation is impregnation. Impregnation occurs when the metal attaches to the oxide. To reach this step, a salt of a corresponding metal oxide is dissolved in water, where the surface is filled with hydroxides, and these hydroxides have the ability to protonate and deprotonate which determines where the metal can attach to the oxide. The proton transfer between the liquid and the surface makes pH shift experiments important in catalyst preparation. After adsorption has occurred, other steps may be followed to create an ideal catalyst.

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## Introduction

Catalysts play a key role in industry which is why catalyst preparation plays a dominant role in catalysis research in the past years. The most preferred preparation method being impregnation, is focused on in the early steps of catalyst preparation. In this step a metal is contacted with an oxide with high surface area in hope to create small metal particles with large surface area. When choosing an oxide to contact with the metal, it must have a large surface area and be compatible with the corresponding metal. The first step would be to determine the point of zero charge (PZC) of the oxide. The PZC is a pH where the net surface charge of the oxide is zero. In solution, when the pH is greater than the PZC, the surface of the oxide is negatively charged and deprotonated. When the pH is less than the PZC, the surface of the oxide is positively charged and protonated. So oxides that are places in solutions with a pH greater than its PZC will absorb cations and oxides contacted with a solution with a pH less than its PZC will absorb anions. The below model can demonstrate the above explanation.

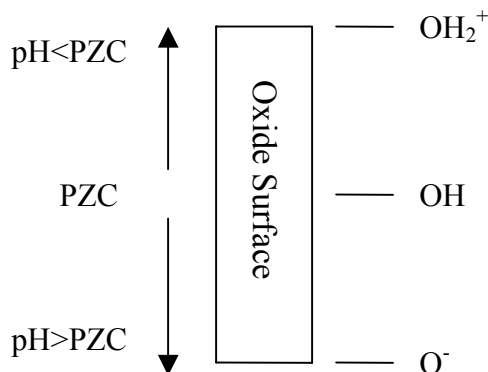


Fig. 1. The point of zero charge model.

In this paper I will discuss the procedure in which I determined the PZC of different oxides and how I used this data to further perform impregnation with a salt containing gold and how I measure the uptake. The main part of this paper will also discuss my future plans with catalyst preparation.

## Methods

The first experiments run were pH shifts for the oxides ceria and zirconia. To do this the mass was calculated using the surface area and surface loadings of the different oxides and the volume that was going to be used. Then the pH of the water was shifted to complete an eleven point pH experiment. These corresponding weights were measured out and contacted with de-ionized, shifted water. After one hour of contact, the final pH was measured and the initial pH versus the final pH was graphed to show the point of zero charge.

Table 1. Data for PZC Experiment #1

	Ceria	Zirconia
Surface Area (m <sup>2</sup> /g)	78	22
Surface Loading (m <sup>2</sup> /L)	500	500
Mass (g)	0.32	1.13

Sample #	Acid/Base added (mL)	Target pH	initial pH	pH final Zr	pH final Ce
1	2.5 10 M HCl	1	1.09	1.09	1.12
2	0.25 mL 10M HCl	2	2.09	2.09	2.12
3	0.25 mL 1M HCl	3	3.01	3.25	3.55
4	0.025 mL 1M HCl	4	3.79	4.7	6.86
5	0.005 mL 1M HCl	5	4.63	6.36	7.89
6	no addition	6	5.72	6.63	8.06
7	0.035 1M NaOH	9	10.27	7.94	9.36
8	0.085 1M NaOH	10	10.59	9	9.86
9	0.25 1M NaOH	11	11.14	9.58	9.8
10	0.25 10M NaOH	12	12.01	11.88	11.92
11	2.5 10M NaOH	13	12.9	12.75	12.81

The second PZC experiment was a three point PZC experiment using alumina with a much higher surface loading than used in the first experiment.

Table 2. Data used for PZC Experiment #2

	Alumina
Surface Area (m <sup>2</sup> /g)	277
Surface Loading (m <sup>2</sup> /L)	100,000
Mass (g)	9.0

Sample #	Acid/Base added (mL)	Target pH	Trial #1	pHi	pHf	Trial #2	pHi	pHf
1	0.2mL 1M HCl	3	1	2.98	7.9	1	2.98	7.78
2	no addition	6	2	6.08	8.04	2	6.08	8.05
3	50 uL 0.1M NaOH	9	3	8.96	8.06	3	8.96	8.08

The third experiment was a pH shift experiment whose purpose was to strengthen pH adjustment skills which are essential for catalyst preparation. The formulas used to determine how much acid or base to add to attain the desired pH are given below.

For an initial pH of 5.00

Target pH 1-5

$$V_{added} = \frac{(V_{initial})(10^{-pH_{target}} - 10^{-pH_{initial}})}{(Conc_{acid} - 10^{-pH_{target}})(1000)}$$

Target pH 6-7

$$V_{added} = \frac{(V_{initial})(10^{-pH_{initial}} - 10^{-pH_{target}})}{(Conc_{base} + 10^{-pH_{target}})(1000)}$$

Target pH 8-13

$$V_{added} = \frac{(V_{initial})(10^{-14+pH_{initial}} + 10^{-pH_{initial}})}{(Conc_{base} - 10^{-14+pH_{target}})(1000)}$$

For an initial pH of 10.00

Target pH 1-6

$$V_{added} = \frac{(V_{initial})(10^{-pH_{target}} + 10^{-(14-pH_{initial})})}{(Conc_{acid} - 10^{-pH_{target}})(1000)}$$

Target pH 7-9

$$V_{added} = \frac{(V_{initial})(10^{-(14-pH_{initial})} - 10^{-(14+pH_{target})})}{(Conc_{acid} + 10^{-14+pH_{target}})(1000)}$$

Target pH 10-13

$$V_{added} = \frac{(V_{initial})(10^{-14+pH_{target}} - 10^{-(14-pH_{initial})})}{(Conc_{base} - 10^{-14+pH_{target}})(1000)}$$

Table 3.Data used for pH adjustment experiment.

Vinitial	30mL			
pHinitial	5.89			
target pH	V added in theory,uL	M of HCl used,mol/L	Vactually added,uL	actual pH
1	303.0263992	10	305	1
2	302.9912652	1	300	1.77
3	302.6399244	0.1	250	2.88
4	299.1265165	0.01	300	3.87
5	26.16141276	0.01	35	5.01
		M of NaOH used,mol/L		
6	0.864662189	0.01	no addition	5.89
7	3.564713008	0.01	4	6.94
8	6.865435199	0.01	9	8.02
9	33.8986473	0.01	45	8.93
10	306.9340896	0.01	300	10.18
11	303.4206817	0.1	300	11.17
12	303.0693409	1	300	12.28
13	303.0342068	10	300	12.88
		M of HNO3 used,mol/L		
1	508.4680258	6	500	1.02
Vinitial	30mL			
pHinitial	10.11			
target pH	V added in theory,uL	M of HCl used,mol/L	Vactually added,uL	actual pH
1	303.4206817	10	304	1
2	306.9340896	1	300	1.71
3	342.0681682	0.1	300	2.75
4	68.71620275	0.1	60	3.87
5	416.8917573	0.01	300	4.65
6	389.5138169	0.01	200	5.94
7	386.1710038	0.01	190	6.93
8	383.4365219	0.01	180	8.01
9	356.1187468	0.01	140	8.97
		M of NaOH used,mol/L		
10	0	1	no addition	10.02
11	263.9924378	0.1	300	11
12	299.1265165	1	300	12.14
13	302.6399244	10	300	12.99
		M of HNO3used ,mol/L		
1	509.1296184	6	500	0.98

In my most recent experiments, I have been testing the uptake of gold onto different oxide supports. These are my main experiments for the summer, and tie all of the skills used for previous experiments together. The first step is to determine the amounts of oxide and gold solution necessary to run the experiment. Then the pH of the gold solution was shifted to the desired pH. After contact with alumina for one hour, the final pH was taken. The next day the ICP (inductively coupled plasma) machine was used to measure the uptake of gold onto the alumina. The following table shows all of the data I have used.

Table 4. Gold onto Alumina Experiment Data

Date: <b>6.14.04</b>									
Au salt: <b>NaAuCl<sub>4</sub>·2H<sub>2</sub>O</b>					Oxide: <b>Al<sub>2</sub>O<sub>3</sub></b>				
Au concentration (ppm): <b>200</b> (1000mL of H <sub>2</sub> O + 408mg of NaAuCl <sub>4</sub> ·2H <sub>2</sub> O)					SA(m <sup>2</sup> /gm): <b>277</b>				
volume of solution adjusted for pH (mL): <b>30</b>					SL(m <sup>2</sup> /L): <b>500</b>				
volume of solution contacted with oxide (mL): <b>25</b>					gms .used: <b>0.045</b>				
ICP label, initial solutions (mm/dd/yy)	Target pH	Amt base or acid/(M)	Actual pH	Actual C <sub>Au1</sub>	Time contacted	Time filtered	pH slurry	Actual C <sub>Au2</sub>	ICP label, final solutions (mm/dd/yy)
A1-1	1	300µL / 10M HCl	0.9	244	1:38	2:38	0.96	102	A2-1
A1-2	2	200µL / 1M HNO <sub>3</sub>	1.95	252	1:52	2:52	1.94	166	A2-2
A1-3	3	no addition	3.04	294	1:51	2:51	3.48	148	A2-3
A1-4	4	220µL / 0.1M NaOH	4.02	313	1:48	2:48	4.32	136	A2-4
A1-5	5	330µL / 0.1M NaOH	5.04	345	1:45	2:45	4.66	118	A2-5
A1-6	6	540µL / 0.1M NaOH	5.98	333	1:44	2:44	5.08	107	A2-6
A1-7	8	600µL / 0.1M NaOH	7.21	343	1:42	2:42	5.42	119	A2-7
A1-8	9	40µL / 0.1M NaOH	7.93	334	1:40	2:40	5.38	109	A2-8

Table 5. Gold onto Zirconia Experimental Data

Date: <b>7.26.04</b>									
Au salt: <b>NaAuCl<sub>4</sub>·2H<sub>2</sub>O</b>					Oxide: <b>ZrO<sub>2</sub></b>				
Au concentration (ppm): <b>200</b> (1000mL of H <sub>2</sub> O + 408mg of NaAuCl <sub>4</sub> ·2H <sub>2</sub> O)					SA(m <sup>2</sup> /gm): <b>22</b>				
volume of solution adjusted for pH (mL): <b>110</b>					SL(m <sup>2</sup> /L): <b>500</b>				
volume of solution contacted with oxide (mL): <b>25</b>					gms .used: <b>0.568182</b>				
ICP label, initial solutions	Target pH	Amt base or acid/(M)	Actual pH	Actual C <sub>Au1</sub>	Time contacted	Time filtered	pH slurry	Actual C <sub>Au2</sub>	ICP label, final solutions
1	1	2000μL / 6M HNO <sub>3</sub>	0.98		11:23	12:35	1.21		2
1	2	200μL / 6M HNO <sub>3</sub>	1.67		11:23	12:35	1.96		2
1	3	no addition	2.91		11:23	12:35	2.99		2
1	4	1200μL / 0.1M NaOH	3.87		11:23	12:35	3.57		2
1	5	1800μL / 0.1M NaOH	4.63		11:23	12:35	4.21		2
1	6	2200μL / 0.1M NaOH	5.94		11:23	12:35	5.74		6
1	7	3000μL / 0.1M NaOH	7.27		11:23	12:35	6.94		2
1	8	3600μL / 0.1M NaOH	10.46		11:23	12:35	8.4		2

Table 6. Gold onto Titania 49 Experimental Data

Date: <b>7.26.04</b>									
Au salt: <b>NaAuCl<sub>4</sub>·2H<sub>2</sub>O</b>					Oxide: <b>TiO<sub>2</sub></b>				
Au concentration (ppm): <b>200</b> (1000mL of H <sub>2</sub> O + 408mg of NaAuCl <sub>4</sub> ·2H <sub>2</sub> O)					SA(m <sup>2</sup> /gm): <b>49</b>				
volume of solution adjusted for pH (mL): <b>110</b>					SL(m <sup>2</sup> /L): <b>500</b>				
volume of solution contacted with oxide (mL): <b>25</b>					gms .used: <b>0.255102</b>				
ICP label, initial solutions	Target pH	Amt base or acid/(M)	Actual pH	Actual C <sub>Au1</sub>	Time contacted	Time filtered	pH slurry	Actual C <sub>Au2</sub>	ICP label, final solutions
1	1	2000μL / 6M HNO <sub>3</sub>	0.98		11:23	12:35	1.11		2
1	2	200μL / 6M HNO <sub>3</sub>	1.67		11:23	12:35	1.9		2
1	3	no addition	2.91		11:23	12:35	2.92		2
1	4	1200μL / 0.1M NaOH	3.87		11:23	12:35	3.41		2
1	5	1800μL / 0.1M NaOH	4.63		11:23	12:35	3.93		2
1	6	2200μL / 0.1M NaOH	5.94		11:23	12:35	5.19		6
1	7	3000μL / 0.1M NaOH	7.27		11:23	12:35	6.47		2
1	8	3600μL / 0.1M NaOH	10.46		11:23	12:35	7.85		2

Table 7. Gold onto Titania 345 Experimental Data

Date: <b>7.26.04</b>									
Au salt: <b>NaAuCl<sub>4</sub>·2H<sub>2</sub>O</b>					Oxide: <b>TiO<sub>2</sub></b>				
Au concentration (ppm): <b>200</b> (1000mL of H <sub>2</sub> O + 408mg of NaAuCl <sub>4</sub> ·2H <sub>2</sub> O)					SA(m <sup>2</sup> /gm): <b>345</b>				
volume of solution adjusted for pH (mL): <b>110</b>					SL(m <sup>2</sup> /L): <b>500</b>				
volume of solution contacted with oxide (mL): <b>25</b>					gms .used: <b>0.036232</b>				
ICP label, initial solutions	Target pH	Amt base or acid/(M)	Actual pH	Actual C <sub>Au1</sub>	Time contacted	Time filtered	pH slurry	Actual C <sub>Au2</sub>	ICP label, final solutions
1	1	2000μL / 6M HNO <sub>3</sub>	0.98		11:23	12:35	1.17		2
1	2	200μL / 6M HNO <sub>3</sub>	1.67		11:23	12:35	1.87		2
1	3	no addition	2.91		11:23	12:35	3.04		2
1	4	1200μL / 0.1M NaOH	3.87		11:23	12:35	3.74		2
1	5	1800μL / 0.1M NaOH	4.63		11:23	12:35	4.3		2
1	6	2200μL / 0.1M NaOH	5.94		11:23	12:35	5.43		6
1	7	3000μL / 0.1M NaOH	7.27		11:23	12:35	6.66		2
1	8	3600μL / 0.1M NaOH	10.46		11:23	12:35	7.68		2

## Results

In the first experiment the PZC was found of ceria and zirconia. Then the results of my experiment were compared to another students experiment to see if they agree. The only difference was that I added an extra ionic solution to my mixture and he did not. The following charts where compiled, showing the PZC of ceria to be about 9.00 and the PZC of zirconia to be about 6.5. A graph was made after contact of one hour and one day and the two graphs show that there was no visible change in the difference of time.

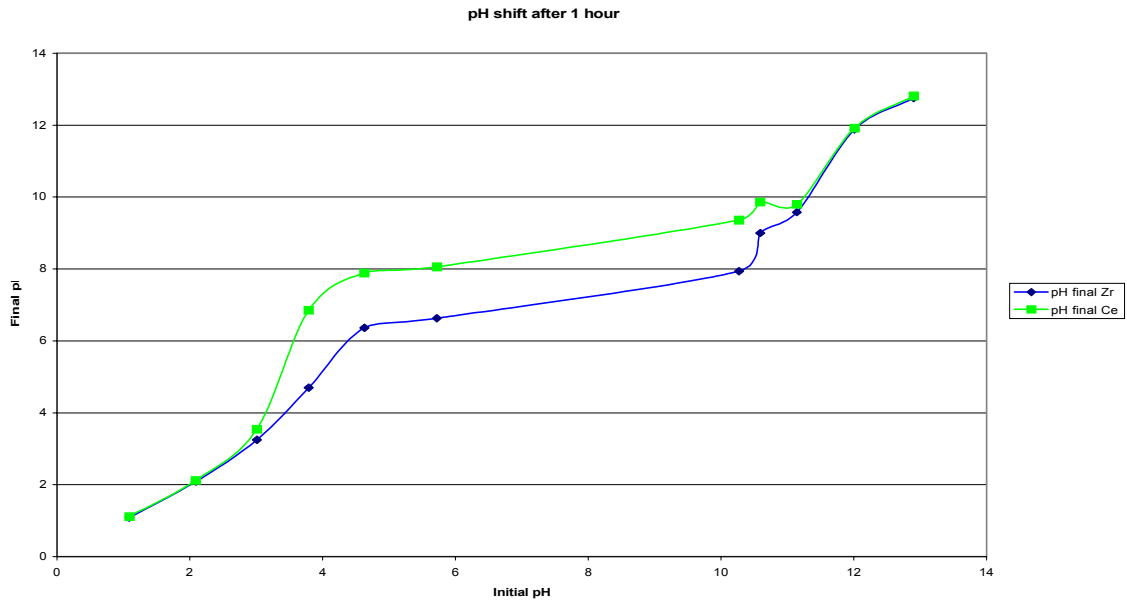


Fig. 2 The pH shift of ceria and zirconia after one hour.

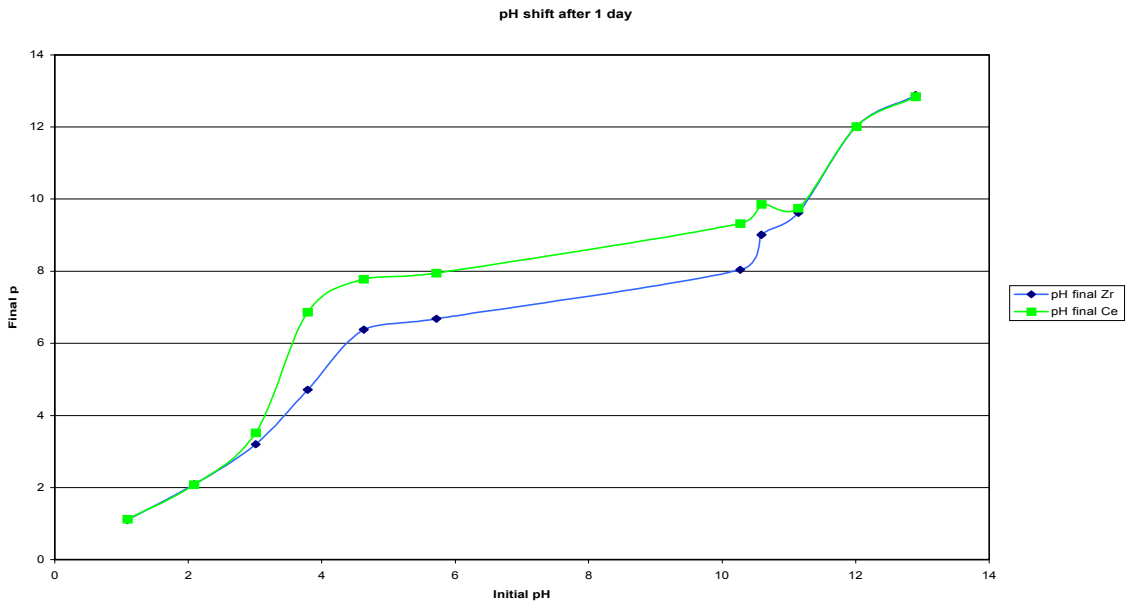


Fig.3 The pH of ceria and zirconia after one day.

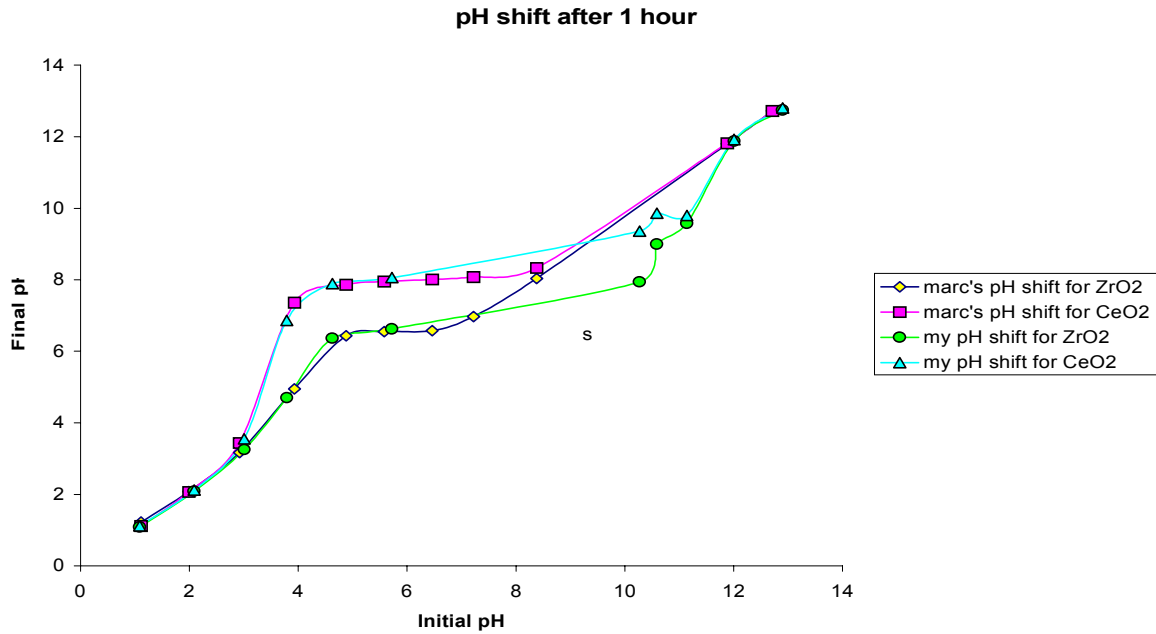


Fig. 4 The pH shift of my results compared to results of another student.

In the second experiment the PZC of alumina was found using 3 points and 11 points. The following graphs show that the PZC of alumina is around 8.00.

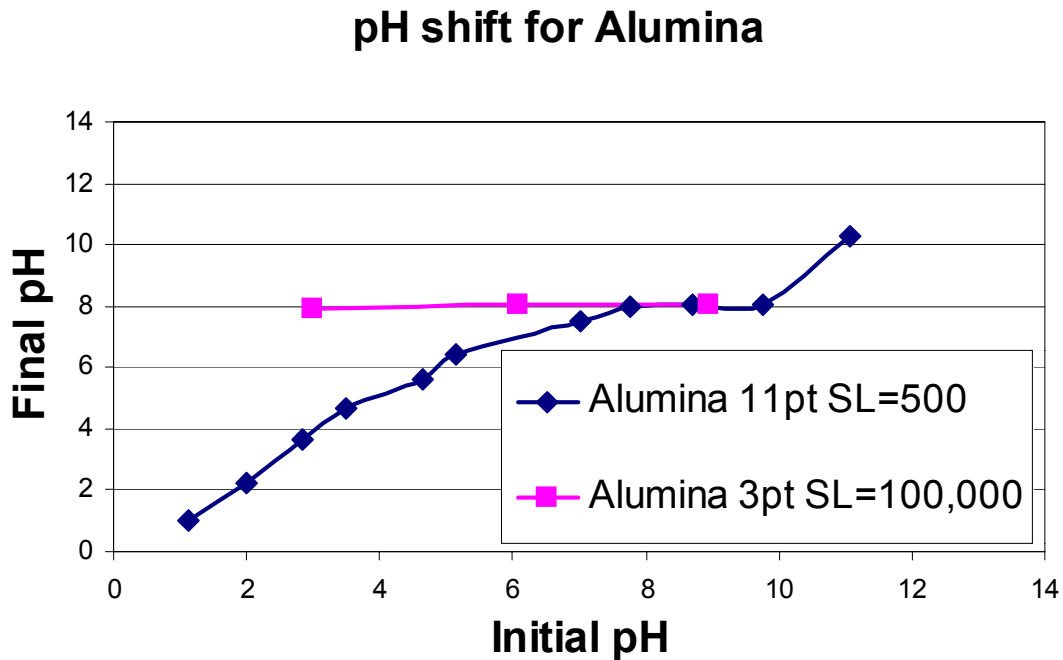


Fig. 5 The pH shift of alumina for 3 and 11 points at different surface loadings.

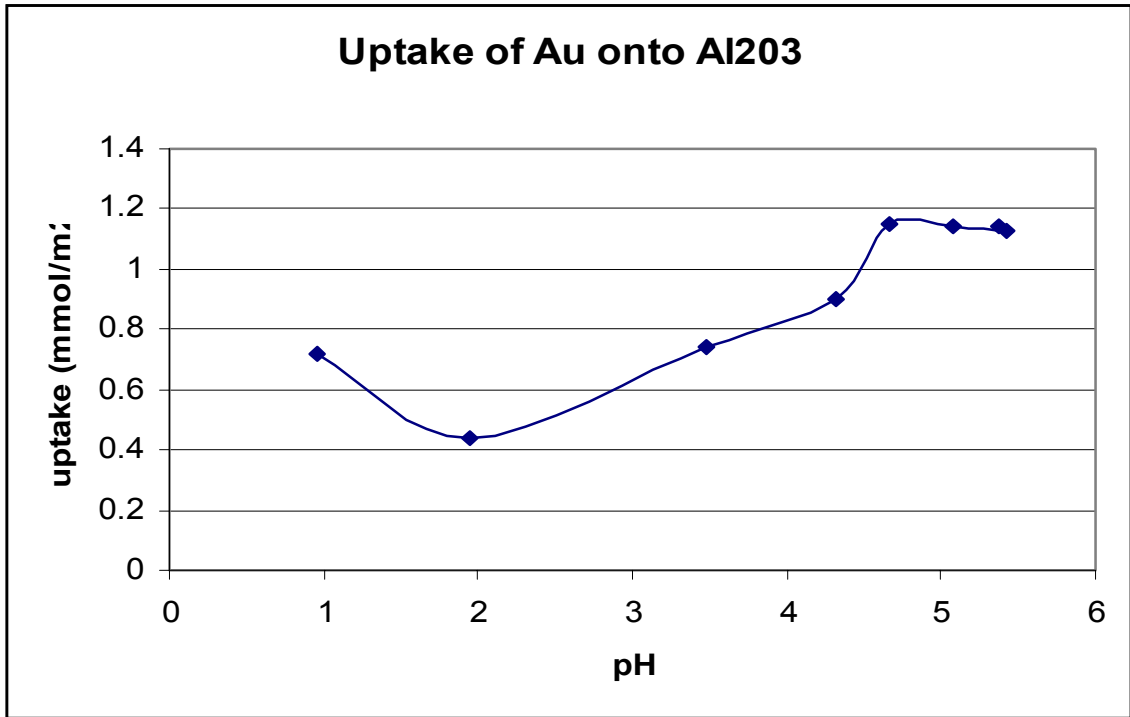


Fig. 6. Uptake of gold onto alumina for Trial #1.

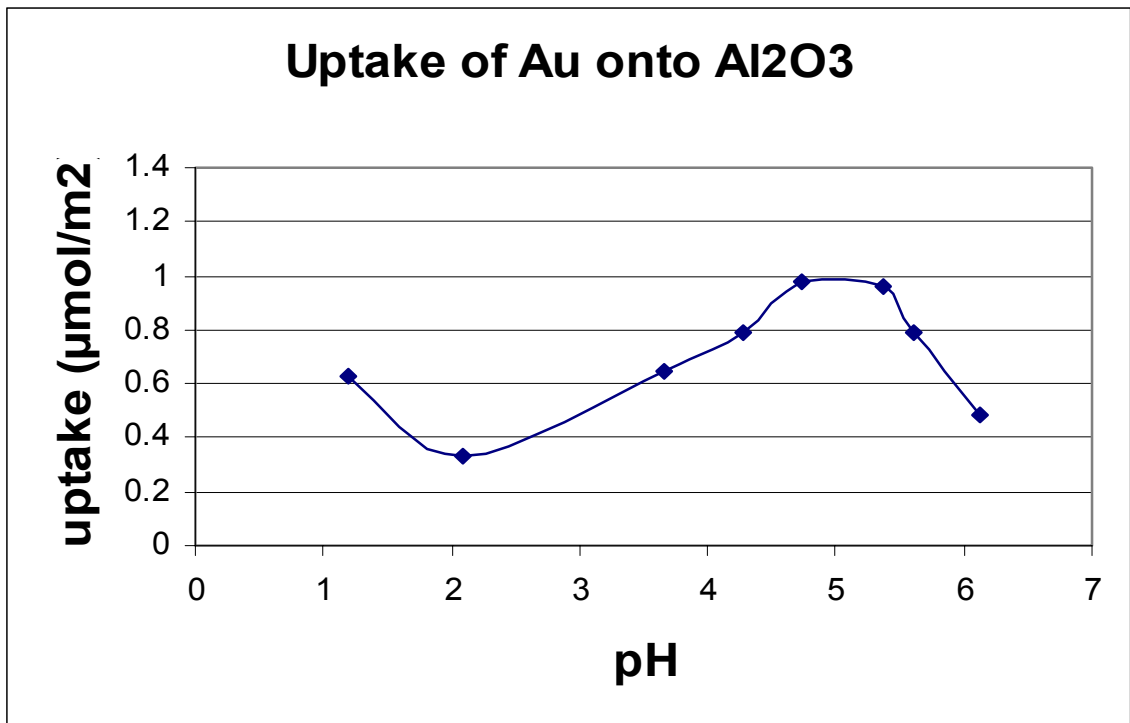


Fig. 7. Uptake of gold onto alumina for Trial #2.

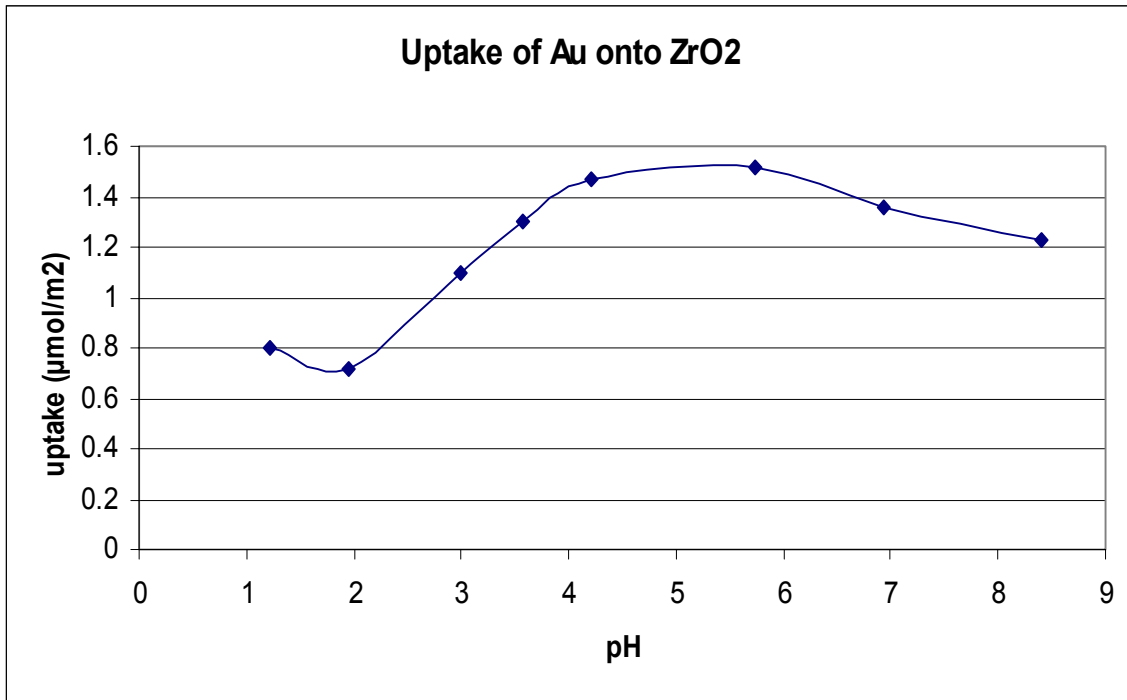


Fig 8. Uptake of Au onto Zirconia

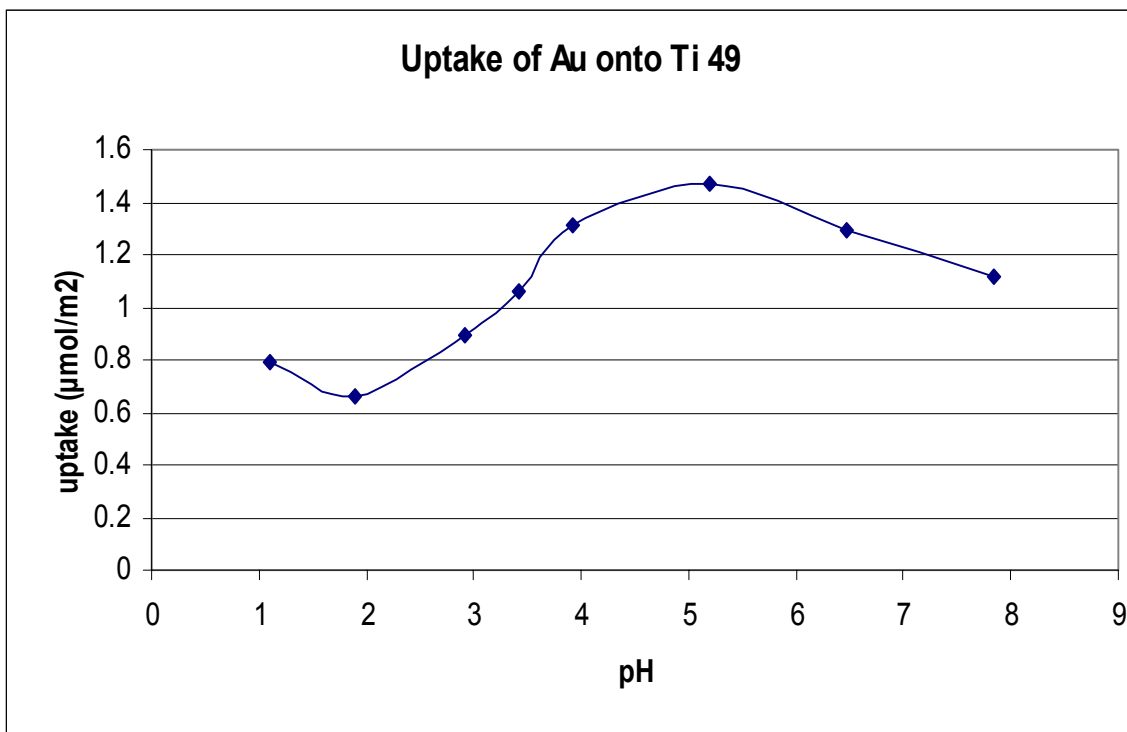


Fig 9. Uptake of Au onto Titania 49

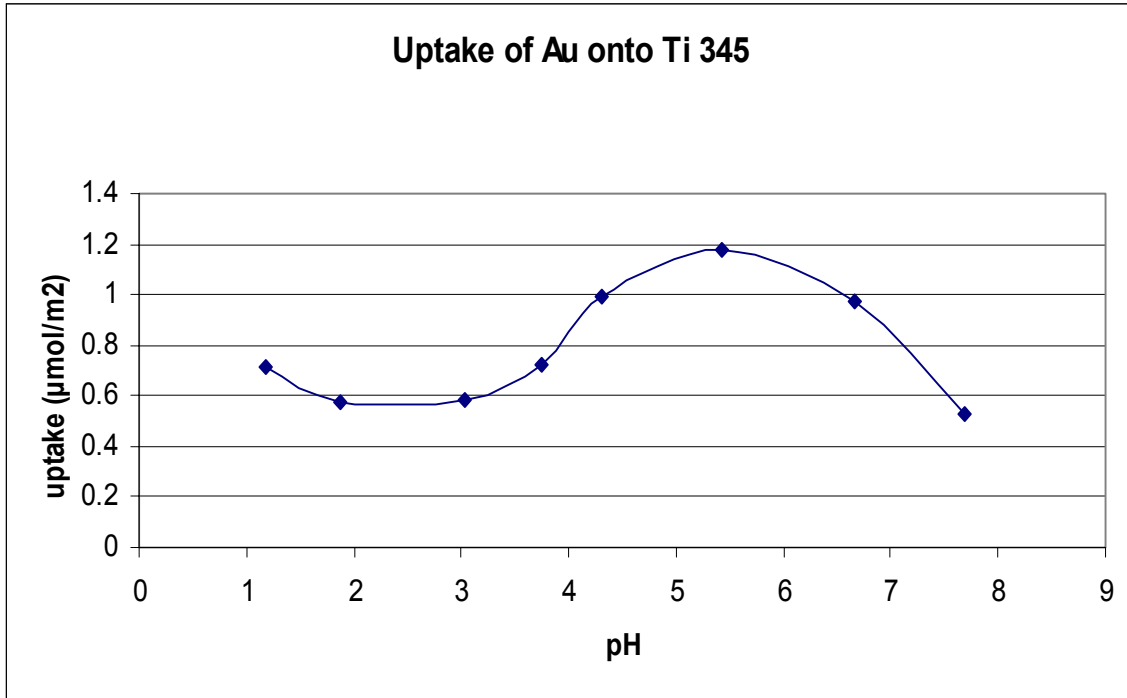


Fig 10. Uptake of Au onto Titania 345

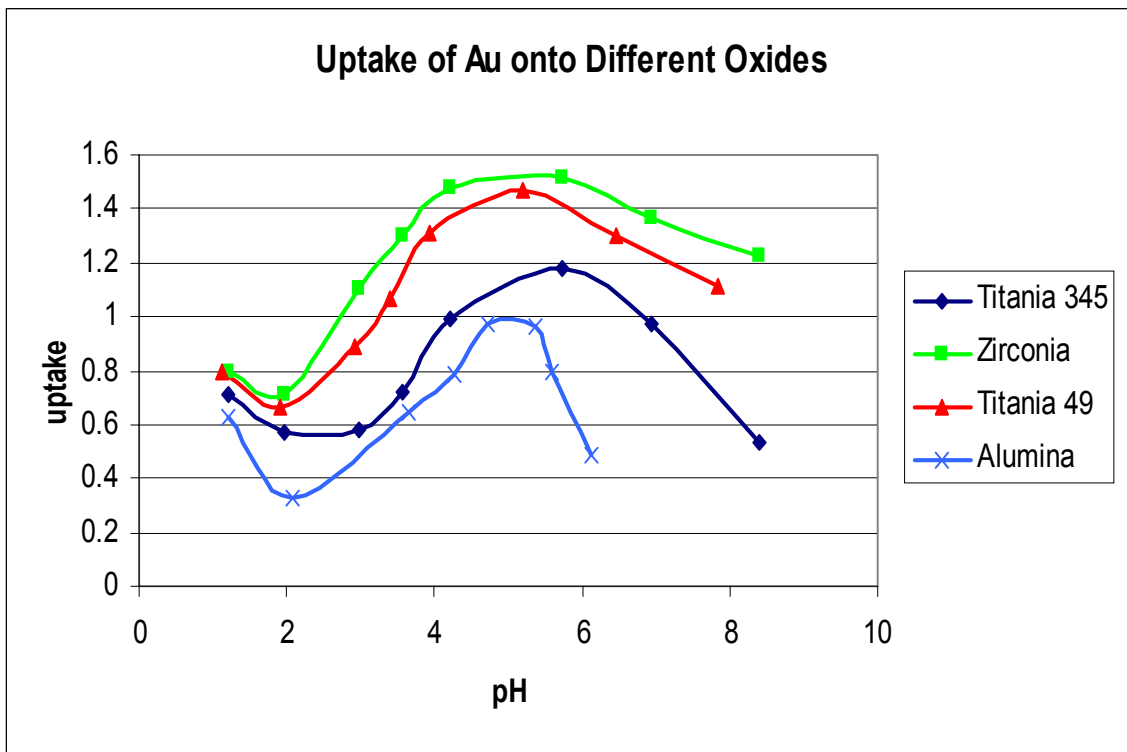


Fig 11. Uptake of Au onto different oxide supports

## **Conclusion**

In conclusion, over the past ten weeks, I have learned a great amount about catalysis. With pH shifts we are able to find the point of zero charge of an oxide, and manipulate solutions in order to find the maximum uptake of metals on oxides. The uptake will differ depending on the different pHs of the solutions, and the different oxides used. My goal is to find the best uptake for different oxides, using the gold solution. Based on my results, about every oxide had a maximum uptake around a pH of 5.00. So in my future experiments I would like to pinpoint a more specific pH and then create a large gold solution, so after I filter the slurry, I can reduce the catalyst and further test for particle size and dispersion.

## **Future Work**

Since I will be doing undergraduate research for Professor Regalbuto in the fall semester, I am adding a future work section to my final paper. I plan to run many more gold experiments with different oxide supports, and possibly even some additional supports. This way I can determine the ideal pH for the maximum amount of uptake for the different supports. Then reducing the gold precursors to form hopefully small metal particles and characterizing the reduced metal particle size with electron microscopy. My last goal will be to find impregnation and reduction conditions for the highest gold dispersion. With higher dispersion, the gold will be more spread out onto the support and therefore more efficient and will be able to react on the surface of the support.

## **Acknowledgements**

I would like to thank my Advisor, Professor Regalbuto for assisting me in my studies, PhD candidates Marc Schreier and Yuhui Zha for helping me conduct experiments and learn how to use the machinery, and graduate student Michael Castorano and Jaime Robles for assisting me in my studies also. I would also like to thank the National Science Foundation (NSF) for financial assistance this summer.

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