

## NDnano Undergraduate Research Fellowship (NURF) 2012 Project Summary

### Instructions

1. **Using this template**, please fill in the five blanks below (name, etc.), and then write two paragraphs summarizing your NURF research:
  - In the first paragraph, describe the problem / problem area and your project goal.
  - In the second paragraph, describe your activities and results. Please include one or two research images, with caption(s).
  - At the end of the summary, be sure to include any papers / posters that were submitted, published or presented as a result of your NURF research.
  - Feel free to add pages.
2. **Review the summary with your faculty mentor before submitting.**
3. When submitting your summary, **please send a separate high-quality digital photo (.jpg) of you in your NURF research/lab environment** for use on the NDnano website and in other NURF promotional materials. If your faculty mentor or a friend is not able to help with the photo, don't hesitate to contact Heidi at 631-0279 or [deethardt.1@nd.edu](mailto:deethardt.1@nd.edu)
4. Please send this completed project summary to Heidi Deethardt at [deethardt.1@nd.edu](mailto:deethardt.1@nd.edu) **no later than the last day of your project. Thank you!**

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- 1) Student name: Bin Wang
- 2) Faculty mentor name: Franklin Tao
- 3) Project title: Synthesis of Nanocatalysts

4) Briefly describe any new skills you acquired during your summer research:

- Synthesis of  $\text{Co}_3\text{O}_4$  nanorods
- Synthesis of supported catalysts with impregnation and deposition-precipitation methods
- Examination of catalytic performance in a fixed-bed flow reactor
- Kinetic study of catalytic water gas shift

5) Please briefly share a practical application/end use of your research:

Design new catalysts which are active for purification of  $\text{H}_2$  source of low temperature fuel cell process. The reaction is called water gas shift which converts  $\text{CO}$  with  $\text{H}_2\text{O}$  into  $\text{CO}_2$  and  $\text{H}_2$ . The practical applications request catalysts active for this reaction at low temperature (room temperature to  $200\text{ }^\circ\text{C}$ ). Search of low temperature WGS has been one of the challenging topics in the community of catalysis.

Begin two-paragraph project summary here:

Search of low temperature water-gas shift reaction ( $\text{CO}+\text{H}_2\text{O}\rightarrow\text{CO}_2+\text{H}_2$ ) has long been one important topic which scientists have made significant efforts in recent years. Understanding catalytic mechanisms is a critical step toward design of new catalysts or optimization of current catalysts. As recent in-situ and operando studies have shown, surface structure and chemistry of catalysts are essentially dynamics, determined by catalysts conditions. Thus, studies of surface chemistry and structure under reaction conditions or during catalysis have been critical for this

purpose. Here we selected  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  as the catalysts. My project mainly focuses on the measurement of catalytic performance of  $\text{Co}_3\text{O}_4$  nanorods supported Pt nanocatalysts for the WGS reaction, the XPS characterization of  $\text{Co}_3\text{O}_4$  nanorods under reaction conditions and the kinetic study.

## **Experiment**

### **Synthesis of $\text{Co}_3\text{O}_4$ Nanorods**

$\text{Co}_3\text{O}_4$  nanorods were synthesized via a hydrothermal method described in Reference [2]. Typically, 2.49 g of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  is dissolved in 30 mL of ethylene glycol and heated to 160 °C to form a homogeneous solution under a constant  $\text{N}_2$  flow. A total of 100 mL of 0.2 M  $\text{Na}_2\text{CO}_3$  aqueous solution is then added to the mixture with the flow rate of 1.11 mL/min through a syringe pump. The precipitation is further aged for 1 h in the mother liquid. After that, the precipitation is gained and thoroughly washed with distilled water and centrifuged for 8 times. It is further washed with ethanol and filtered, followed by drying at 50 °C overnight under vacuum. Finally, the dried precipitation is calcined at the temperature of 250 °C for 4 h.

### **Synthesis of $\text{Co}_3\text{O}_4$ Nanorods Supported Pt Nanocatalysts**

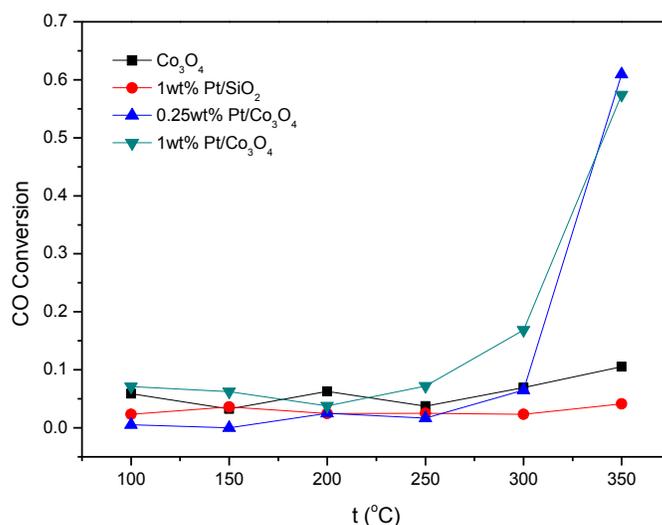
The synthesized  $\text{Co}_3\text{O}_4$  nanorods are sifted to get  $\text{Co}_3\text{O}_4$  powder that is under 80 mesh. The Deposition-Precipitation method is used to synthesize  $\text{Co}_3\text{O}_4$  supported nanocatalysts with different Pt loadings.  $\text{SiO}_2$  supported Pt nanocatalyst is also synthesized via impregnation method to perform as the comparison with the  $\text{Co}_3\text{O}_4$  supported nanocatalysts.

### **Characterization**

$\text{Co}_3\text{O}_4$  nanorods are characterized with In-Situ XPS.

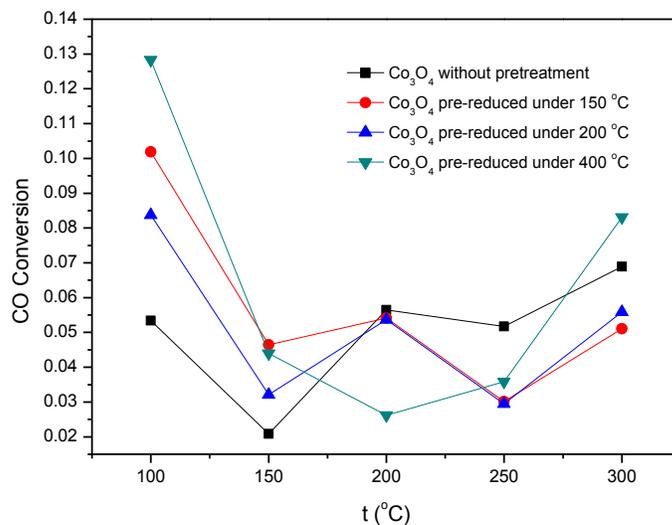
## **Results and Discussions**

Catalytic performance of  $\text{Co}_3\text{O}_4$  supported nanocatalysts with different Pt loadings and the  $\text{SiO}_2$  supported Pt nanocatalyst is shown in Figure 1. We can see from the figure that 1 wt% Pt/ $\text{Co}_3\text{O}_4$  possesses excellent activity under the temperature of 350 °C. However, 1 wt% Pt/ $\text{SiO}_2$  is almost totally inactive under the same condition. From the previous study on the microstructure of  $\text{Co}_3\text{O}_4$ , we know that there is much oxygen vacancy in the crystal, which  $\text{SiO}_2$  does not have. Thus, we can conclude that the oxygen vacancy in the structure of the nanocatalysts will enhance the catalytic activity in the WGS reaction. That is to say, we can suppose that oxygen vacancy is exactly where the WGS reaction takes place.



**Figure 1.** Catalytic Performance of Different Nanocatalysts  
 Reaction conditions: 10 vol% CO/ 10.00uL•min<sup>-1</sup> H<sub>2</sub>O; 30000mL/(g•h)

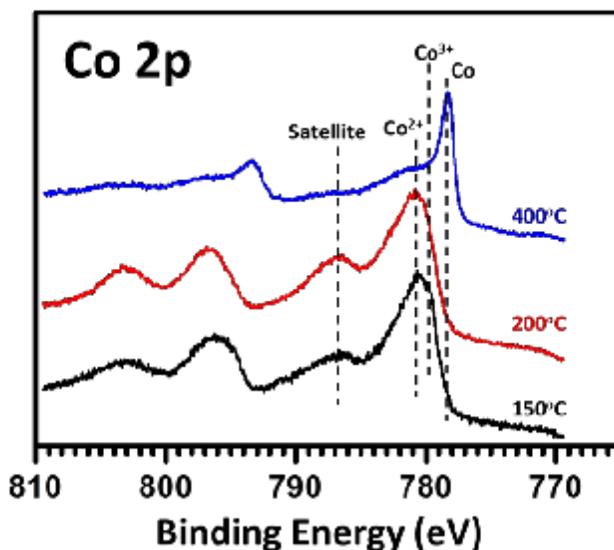
Figure 2 shows the catalytic performance of Co<sub>3</sub>O<sub>4</sub> nanorods without pretreatment and Co<sub>3</sub>O<sub>4</sub> nanorods pre-reduced under different temperatures in a constant flow of H<sub>2</sub> for 1h.



**Figure 2.** Catalytic Performance of Co<sub>3</sub>O<sub>4</sub> Reduced under Different Temperatures  
 Reaction conditions: 10 vol% CO/ 10.00uL•min<sup>-1</sup> H<sub>2</sub>O; 30000 mL/(g•h)

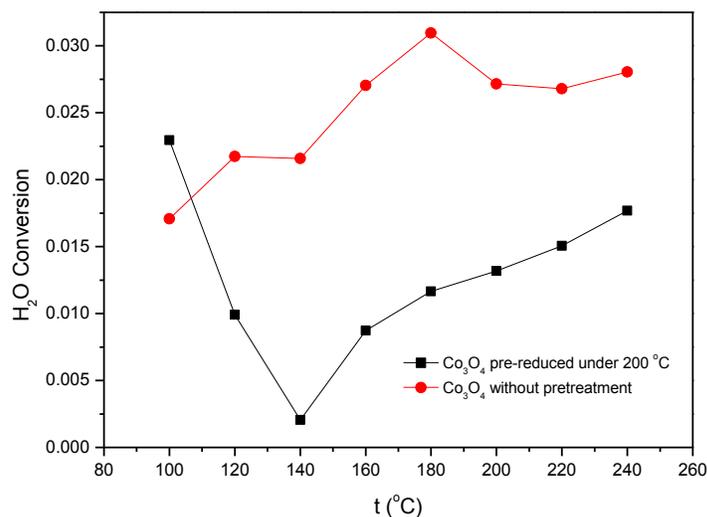
We can easily conclude from the result that the pre-reduced samples are all more active than the Co<sub>3</sub>O<sub>4</sub> nanorods without pretreatment in the WGS reaction. And moreover, the pre-reduced samples all showed their highest activity under the very temperature of 100 °C. The surface

chemistry of the catalysts under pretreatment conditions was characterized via AP-XPS, as shown in Fig. 3. The photoemission features of Co 2p show satellite peaks at  $\sim 786.7$  eV at  $150^\circ\text{C}$ , which demonstrates the formation of CoO as a result of the partial reduction of  $\text{Co}_3\text{O}_4$ . The intensity of satellites is strengthened at  $200^\circ\text{C}$ . Notably, a slight split of Co  $2p_{3/2}$  main peak can be observed at  $150^\circ\text{C}$ , with  $\text{Co}^{3+}$  at  $\sim 779.8$  eV and  $\text{Co}^{2+}$  at  $\sim 780.8$  eV, respectively, which indicates  $\text{Co}_3\text{O}_4$  is partially reduced to CoO at  $150^\circ\text{C}$  followed by a complete reduction to CoO at  $200^\circ\text{C}$ . At  $400^\circ\text{C}$ , the Co  $2p_{3/2}$  main peak appears at  $\sim 778.3$  eV attendant with the disappearance of satellites and  $\text{Co}^{2+}$ , consistent with the formation of metallic cobalt, which demonstrates the complete reduction of cobalt oxide to metallic cobalt. In correlation with the catalytic data,  $\text{Co}^{2+}$  or even Co metal may be the true active phase of the catalyst in the WGS reaction. This is also consistent to the conclusion we gained just now with the comparison of  $\text{Co}_3\text{O}_4$  nanorods and  $\text{SiO}_2$  as  $\text{Co}^{2+}$  or Co always contains more oxygen vacancy in their surface structures. Thus we can assume that the reason why the pre-reduced samples can have the best activity under the very temperature of  $100^\circ\text{C}$  is that in the process of WGS reaction  $\text{Co}^{2+}$  or Co can easily be oxidized by some reagent in the reaction (and it can only be  $\text{H}_2\text{O}$ ) to  $\text{Co}^{3+}$  and therefore the activity loses.



**Figure 3.** Photoemission features of Co 2p under different pretreating temperatures. The gas during data acquisition is 0.5 Torr  $\text{H}_2$

Kinetic study of the catalyzed WGS reaction over  $\text{Co}_3\text{O}_4$  nanorods and the pre-reduced  $\text{Co}_3\text{O}_4$  nanorods is done under the CO and  $\text{H}_2\text{O}$  ratio of 3:1. The results are shown in Figure 4. The activation energy  $E_a$  of pre-reduced  $\text{Co}_3\text{O}_4$  catalyzed WGS reaction can be calculated using the kinetic study data of  $160\sim 240^\circ\text{C}$  as  $15.5$  kJ/mol. Moreover, by comparing the conversion of CO and production of  $\text{H}_2$  in the kinetic study data of pre-reduced  $\text{Co}_3\text{O}_4$ , it is interesting to find that only under  $100^\circ\text{C}$ , the conversion of CO is higher than the production of  $\text{H}_2$  that should be got from the corresponding CO, suggesting that some byproduct has been attained from CO. However, under all the other temperatures, the conversion of CO is always lower, indicating that  $\text{H}_2$  is produced via some other reactions. This is consistent with our assumption that the  $\text{Co}^{2+}$  phase is gradually oxidized by  $\text{H}_2\text{O}$  and the product of the oxidization is just  $\text{H}_2$ .



**Figure 4.** Kinetic Study of Co<sub>3</sub>O<sub>4</sub> and Pre-reduced Co<sub>3</sub>O<sub>4</sub>  
 Reaction conditions: 99.9 vol% CO/ 10.00uL•min<sup>-1</sup> H<sub>2</sub>O; 12000 mL/(g•h)

## Conclusions

We can primarily conclude from all the experiments that the WGS reaction takes place in the oxygen vacancy of the Co<sub>3</sub>O<sub>4</sub> nanorods and the real active phase of Co<sub>3</sub>O<sub>4</sub> nanorods should be Co<sup>2+</sup> generated in the process of WGS reaction below 400 °C. Further characterizations are needed to provide stronger evidence to substantiate our conclusion.

## References

- [1] C. Rhodes, G. J. Hutchings, A. M. Ward, *Catal. Today*, 1995, **23**: 43-58.
- [2] X. Xie, P. Shang, Z. Liu, Y. Lv, Y. Li, W. Shen, *J. Phys. Chem. C*, 2010, **114**: 2116-2123.

Publications (papers/posters/presentations):