In-Situ Observation: from Mononuclear Species to Metal Clusters and then to Metal Nanoparticles

Yan N. and Kou Y.*
PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R .China
*yuankou@pku.edu.cn

Introduction

The active center of many heterogeneous catalysts applied in industry is of nanoscale. However, the details of the formation of these nanoparticles are not fully understood. Recently a new branch in heterogeneous catalysis, the so-called quasi-homogenous reactions, raises considerable attention and proved to be very successful for a variety of reactions [1]. The catalysts used in such systems generally composed of metal nanoparticles in the presence of a soluble stabilizer. Such an approach not only brings new possibilities for catalytic system design, but also facilitates in-situ observations because of its “homogenous” property that allows direct implementation of techniques used in homogenous catalysis. Poly-1-vinyl-pyrrolidin-2-one (PVP) is one of the most widely used stabilizers for soluble metal nanoclusters (Ru, Rh, Pd, Pt, Cu, et. al.) synthesis. Herein, we would like to communicate our in-situ observation on the growth of PVP/PVP derivatives stabilized Pt and Fe nanoparticles.

Materials and Methods

Poly-3-Octyl-1-vinyl-pyrrolidin-2-one (C_8-PVP) was prepared in a way developed in this lab and all other chemicals were purchased from commercial sources. In-Situ IR was determined in a home-made cell over Bruker Vector 27. In-Situ UV-Vis data were obtained in a Cary 1E spectrometer. In-Situ time-resolved energy-dispersive XAFS measurement was made at SPring-8 synchrotron radiation facility. TEM analysis was performed on a Hitachi H-9000 HRTEM at 300 keV.

Results and Discussion

In-situ techniques studies were applied to two systems. One is the formation of Pt nanoparticles in the presence of PVP in ethanol/water solution from H_2PtCl_6, the other is the thermal decomposition of Fe $(CO)_5$ to form Fe nanoparticles in squalane stabilized by C_8-PVP. The key observations and results are:

1) The formations of these nanoparticles are relative slow processes, thus are particularly suitable for in-situ techniques with resolution ability at second scale. For example, the entire process for the formation of Pt nanoparticles took about 1 hour (see Figure 1a).

2) The formation of metal nanoparticles consisted of several stages, including the formation of zero valent metal atoms, the aggregation of free metal atoms to clusters and the growth of clusters into particles. For Pt nanoparticles, the first step happened during 28th to 33th min, as evidenced by the pictures in Figure 1a and in-situ UV data in Figure 1b. Once the free atoms were formed, they began to aggregate into small clusters (diameter less than 1 nm), which means the formation of free metal atoms and the small clusters happens contemporary. At this stage, no nano scale material can be detected by TEM. However, in-situ XAFS demonstrated an increase of the coordination number evaluated by the curve fitting of the Pt-Pt or Fe-Fe bond. Also, in-situ IR observed the evidence for the presence of iron carbonyl clusters at this stage in $Fe(CO)_5$’s case, further supporting the presence of small clusters as intermediate in the formation of nanoparticles. The final stage is the aggregation of small nanoclusters into nanoparticles (several nanometers size). At this stage, neither in-situ UV nor in-situ XAFS can detect mononuclear species in the system while the coordination number of Pt-Pt or Fe-Fe kept growing. The final size of the nanoparticles was about 4-5 nm by TEM analysis. By detecting the IR spectrum of the final CO absorbed on Fe nanoparticles, in-situ IR gave some additional structural information on the Fe nanoparticles.

Significance

Up to now, mechanism on the formation of PVP stabilized nanoparticles and the structures of these particles remain elusive although they are crucial to understand their catalytic behaviors and are of general interests to researchers in catalysis and nanomaterial science. We elucidated some aspects concerning the fundamental steps of the growth of PVP stabilized nanoparticles by in-situ IR, UV-Vis and XAFS techniques. An evolution from mononuclear species (non-zero valent) to zero valent metal atom, then to metal clusters and finally aggregated to metal particles was proposed.

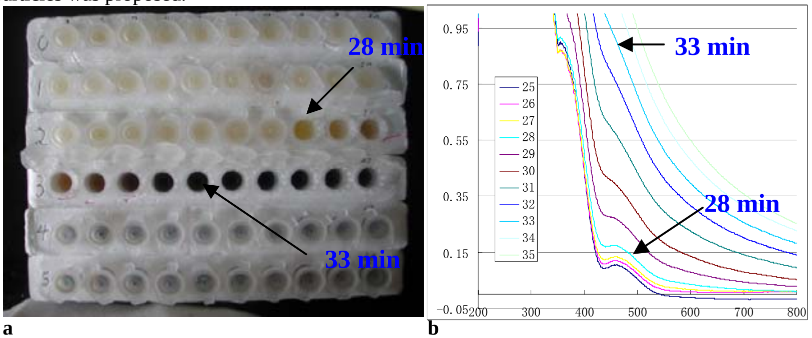

Figure 1. (a) Pictures of the samples of the formation of Pt nanoparticles from H_2PtCl_6 in the presence of PVP in ethanol/water. The time difference of each sample is 1 minute. (b) In-situ UV-Vis data of the same process (data from 25 min to 35 min).

References

1. For some recent examples for the application quasi-homogenous catalysis in our lab, please see: a. Yang, X., Yan, N., Fei, Z., Crespo-Quesada, R., Laurenczy, G., Kiwi-Minsker, L., Kou, Y., Li, Y., Dyson, P. J. *Inorg. Chem.* 47, 7444 (2008). b. He, L., Liu, H., Xiao, C., Kou, Y. *Green Chem.* 10, 619 (2008). c. Xiao, C., Cai, Z., Wang, T., Kou, Y., Yan, N. *Angew. Chem. Int. Ed*. 47, 746 (2008). d. Zhao, C., Gan, W., Fan, X., Cai, Z., Dyson, P. J., Kou, Y. *J. Catal*. 254, 244 (2008). e. Wang, T., Xiao, C., Yan, L., Xu, L., Luo, J., Shou, H., Kou, Y., Liu, H. *Chem. Comm*. 42, 4375 (2007). f. Zhao, C., Wang, H., Yan, N., Xiao, C., Mu, X., Dyson, P. J., Kou, Y. *J. Catal.* 250, 33 (2007). g. Yan, N., Zhao, C., Luo, C., Dyson, P. J., Liu, H., Kou, Y. *J. Am. Chem. Soc.* 128, 8714 (2006). h. Mu, X., Meng, J., Li, Z., Kou, Y. *J. Am. Chem. Soc.* 127, 9694 (2005)