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Synthesis and Application of Nano-Structured Metal Catalysts

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Summary

Nanoscience has evolved as a major research trend from an ongoing effort to miniaturize processes from using micro-systems to the nanoscale. Towards this end, it is well admitted that the ‘bottom-up’ approach should now replace the classic ‘top-down’ one, a strategic move that is common to several areas of application of nanoscience, including optics, electronics, medicine and catalysis. The latter discipline certainly is the key one for the development of starting chemicals, fine chemicals and drugs from raw materials. The catalysts for these processes are usually homogeneous organometallic complexes laborious to synthesize and/or air sensitive. Moreover, their stability is a major concern and separation from the product mixture is often difficult and costly. Alternatively, it is possible to use metal nanoparticles to catalyze these reactions. The aim of this thesis has been to develop new methods to synthesize more ‘atom- economical’ and ‘selective’ cluster catalysts.

Chapter 1 starts with a general introduction into the field of metal nanoparticles involving synthetic pathways, stabilizing mechanism, and their application as catalysts in various reactions. Overviews on the research concerning transition metal catalyzed-Ullmann and Hiyama couplings, click chemistry is also presented.

Chapter 2 deals with application of Cu nanoclusters as catalysts in the “click” cycloaddition of azides with terminal alkynes to give the corresponding 1,4-disubstituted 1,2,3-triazoles. No additional base or reducing agent is needed. The products are isolated in good yields (80–99%) and high selectivity. The clusters are simple to prepare, stable and can be applied to a variety of azide and functionalized alkynes. The question of whether Cu clusters are the actual catalysts or “mere reservoirs” for Cu species in the so-called ‘cluster-catalyzed cross-coupling’ is also discussed. We examined the reaction kinetics and function of Cu clusters by comparing the activity with different Cu catalysts. The higher activity of metal clusters in the cycloaddition reactions led us to think that if catalysis occurs on the clusters’ surface. The mechanism is complex but there are evidences that a Cu^{I} -alkyne intermediate is involved.

Controlling the cluster structure when two metals are combined may tune the catalytic activity and improve the “catalyst atom economy”. This was the main motivation behind chapter 3. In this chapter, core/shell metal nanoclusters are synthesized by a novel combined

chemical/electrochemical method. The Ni core is prepared electrochemically and, then, Pd shells are grown on the Ni clusters by chemical reduction. The resulting clusters are used as catalysts in the Hiyama cross-coupling reaction. The Ni/Pd catalyst is applied to a range of iodo- and bromoaryl substrates, and gave high yields and selectivity. For the same amount of palladium, the activity of Ni/Pd clusters is higher than the pure Pd or the pure Ni clusters and, the alloy bimetallic Ni/Pd ones. This indicates an efficient use of the surface Pd atoms.

In chapter 4, we present a room temperature and electroreductive alternative to the Ullmann reaction. The Pd clusters catalyst is generated *in situ* by electrochemistry. The system gives good yields in the homocoupling reaction of iodo- and bromoaryl substrates. Only electricity and water are necessary to close the catalytic cycle and regenerate the Pd⁰. The kinetic studies made us propose a two-electrons mechanism involving a radical anion that coordinates at the surface of the Pd nanoparticles. The advantages of using ionic liquids as solvent and cluster stabilizer, is also described. The solvent is reusable for at least five consecutive reaction cycles.

In chapter 5, besides my main project on cluster catalysis, I studied the synthesis of new materials. We show a simple and general method to entrapped chiral molecules in a porous Pd matrix. The system's crystal structure is also studied in detail. UV-visible and electron photoemission spectroscopies show that the "doped" Pd and the "imprinted" Pd can distinguish between enantiomers. The catalytic applications of these materials in enantioselective hydrogenation reactions are also presented.

Conclusion and outlook

We have shown that metal nanoclusters are highly effective catalysts for different reactions, from homo- and cross-coupling to click chemistry. They display unique catalytic properties that are different from traditional homogeneous and heterogeneous catalysts. This is mainly due to the large number of co-ordinatively unsaturated surface atoms, which can lead to high catalytic activity *via* surface reaction. Moreover, we have presented new methods that make their synthesis simple, efficient and more environmentally-friendly; with possibility also to easily tailor their structure and composition.

At this point, the design and use of metal nanoparticles is well advanced. A large variety of nanoparticles preparation methods and materials are available, as well as modern

characterization techniques. These advances have considerably improved the selectivity of nanoparticles-catalyzed reactions. Moreover, there is a growing call for more mechanistic studies to understand the real nature of cluster catalysis. The recycling and efficient re-use, without loss of activity of the metal clusters, remains a challenge and should be the subject of highest priority for future research.

