Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

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Bowl-shaped π-conjugated compounds including partial structures of the fullerenes, which are called "buckybowls," are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. Very few buckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiral bowls has appeared. In this project, we develop the rational route to the various buckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.

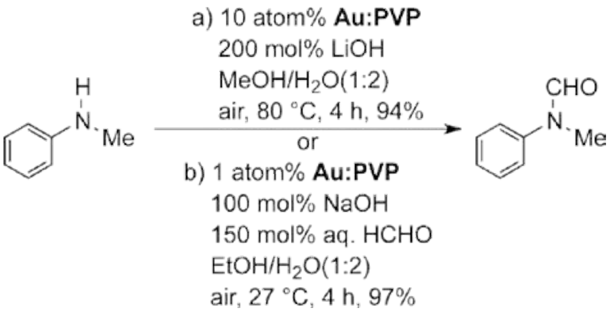
1. The Impact of Basis Set Superposition Error on the Structure of π-π Dimers[1)]

The effect of basis set superposition error (BSSE) on the structure and energy of benzene, naphthalene, corannulene, and sumanene dimer has been analyzed. MP2 method was chosen and the effect is estimated using 6-31G, 6-31G(d), 6-311.G(d), cc-pVDZ, and cc-pVTZ basis sets. The model calculations on benzene dimer indicate that the impact of BSSE on the equilibrium geometry of π-stacked dimers appears to be quite significant. Calculations on larger molecular dimers such as the dimers of naphthalene, corannulene, and sumanene are also studied. Our results cautions that whenever a counterpoise correction is significant for the stacking interaction, it is essential to incorporate the BSSE in the geometry optimization. The most often adopted practice of including the BSSE only for the energy and not for the geometry may be not be acceptable for stacking interactions. The impact of BSSE on structure and energy is much higher as the size of the monomeric units of stacked π-dimers is increased. The results on the stacking interactions of the two prototypical buckybowls, corannulene, and sumanene reveal that most of the pragmatic basis sets are essentially associated with a very high correction due to BSSE.

2. *N*-Formylation of Amines Catalyzed by Nanogold Under Aerobic Oxidation Conditions with MeOH or Formalin[2)]

Direct formation of amides from alcohols or aldehydes with amines has recently received attention from the viewpoint of the development of environmentally benign process. In particular, *N*-formylation of amines using MeOH or formaldehyde (especially formalin) is very important. The use of simple reactants makes it possible to understand the reaction mechanism. Furthermore, the starting materials are both economical and the formamide derivatives produced in the reaction are important intermediates in organic synthesis. Until now, though, only a few examples of this transformation have been reported. Cu hydroxyl salts have been used in the presence of hydrogen peroxide. However, aerobic oxidation has been achieved with nanosize-gold supported on metal oxide with MeOH, and formylation of dimethylamine with formaldehyde has been carried out using metallic gold or silver surfaces as a catalyst. Practical procedures for *N*-formylation by aerobic oxidation that tolerate a wide scope of amines are still needed.

Nanosized-gold metal has recently attracted a great deal of interest because of its high activity and potential application in the emerging area of green oxidation chemistry. We have recently demonstrated that gold nanoclusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (**Au:PVP**) act as an excellent quasi-homogenous catalyst for the aerobic oxidation of benzylic alcohols, generation of H_2O_2 in the presence of ammonium formate, homo-coupling reaction of arylboronic acids, and other cyclization reactions. **Au:PVP** was found to be an excellent catalyst for the direct *N*-formylation of amine with MeOH or formalin as a formyl source. In particular, only 1 atom% of catalyst was needed and the reaction proceeded under ambient conditions in the reaction with formalin solution. The results strongly indicate that **Au:PVP** might possess superior catalytic activity toward the oxidation of hemiaminal intermediate when compared to other catalysts. Such characteristic features of **Au:PVP** will be applicable to many types of practical organic syntheses.we wish to report highly selective direct *N*-formylation using MeOH or formalin as a formyl source in the presence of **Au:PVP** under aerobic conditions.



3. Chitosan-Stabilized Gold, Gold–Palladium, and Gold–Platinum Nanoclusters as Efficient Catalysts for Aerobic Oxidation of Alcohols[3)]

Chitosan was used as a stabilizer for the synthesis of Au, AuPd and AuPt nanoclusters (NCs). The produced NCs had a narrow particle size distribution with sizes less than 2.3 nm in diameter and were characterized by various techniques such as UV-Visible spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and scanning electron microscope energy dispersive spectroscopy (STEM-EDS). These metal NCs exhibited high catalytic activity toward the aerobic oxidation of various alcohols under ambient conditions comparable with the reported **Au:PVP** catalyst. Au NCs protected by chitosan could easily be recovered for repeated use.

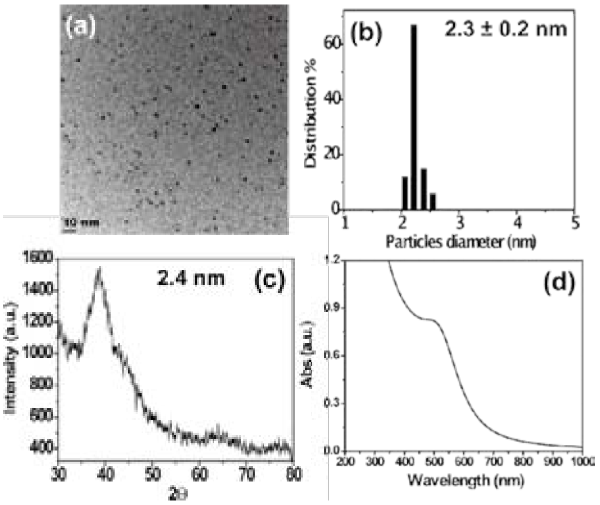


Figure 1. (a) TEM image of chitosan-stabilized Au NCs. (b) Particle size histogram plot obtained from (a). (c) X-ray diffraction pattern of Au:Chit. (d) UV-Visible spectrum of Au:Chit.

4. Magnetically Recoverable Magnetite/Gold Catalyst Stabilized by Poly(*N*-vinyl-2-pyrrolidone) for Aerobic Oxidation of Alcohols[4)]

Fe_3O_4:PVP/Au nanocomposite synthesized *via* a two-step procedure was tested as quasi-homogenous catalysts in alcohol oxidation. It was found that the nanocomposite was able to carry out aerobic oxidation of alcohols in water at room temperature. Studies show rapid magnetic recoverability and reusability characteristics.

References

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