Overview of two lectures

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Catalysis is widely used in human life. Historically, two catalysts, heterogeneous catalysts by metal particles on the surface of solid supports and homogeneous catalysts by organometallic complexes, have been investigated in terms of physical chemistry and related to organic, organometallic, and coordination chemistry, respectively. The former is the reactions occurring on the surface of metals and typically used for decomposition of pollutants from exhaustive gases, whereas the latter is the reactions promoted by molecular species and is a powerful tool for production of functional molecules and materials. In my two successive lectures at Ajou University, I would like to deliver the audience how basic science considering net catalyst species is interesting and how outcomes of the basic research are applied to technology in industry by collaboration of academia and industry. It should be noted that catalysts are the materials which realize the reactions with lower activation energy. The reaction occurs through several elementary reactions, and the initial species is regenerated at the end of the catalysis and restart another run of the catalytic cycle. Consequently, only a tiny amount of catalysts works for the conversion of starting materials to the products. From industrial point-of-view, catalysts and catalysis is a key technology to make the modern society green with reasonable cost.

***Definition of “Catalyst”***

A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself in the process.

1. Uncatalyzed reactions
2. Catalytic reactions
3. Unsuccessful reactions, where catalytic species becomes inactive during the reactions

Preparation and applications of transition metal nanoparticles

supported by hyperbranched polymers

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Recent advance in nanoscience urged to develop boundary area between heterogeneous catalysis using bulk metals and homogeneous catalysts employing molecular metal complexes. Nao-sized metal particles are generally unstable and easily aggregates to form larger metal particles. Several reagents which stabilize the metal nanoparticles are reported, and organic ammonium salts are one of them, and polymers having polar functional groups are another one. Collaborations with Nissan Chemical Co. Ltd. realized easy access to hyperbranched polystyrenes (HPS) with dithiocarbamate (DC) groups at the end group. Hyperbranched polymers are one of the dendric polymers, and show unique properties from pseudo-spherical structures, random branching polymer architectures, and existence of many functional groups. We have achieved chemical modification of DC groups of HPS-DC to ammonium salts, which provided synthetic procedures for HPS-NR3+Cl- in industrial scales. Of interest is its unique dispersibility to various solvents, which can be controlled by changing the R group. We found that ammonium salts in HPS-NR3+Cl- behaved as good functional groups to stabilize transition metal nanoparticles. Treatment of HPS-NR3+Cl- with certain organometallic precursors or reactions with metal salts in the presence of reducing reagents resulted in well-dispersed metal nanoparticles of 1~4 nm size. Dispersibility of the resulting M@HPS-NR3+Cl- was dependent on the R groups. TEM analyses suggested the metal particles are surrounded by several molecules of HPS-NR3+Cl-. We utilized M@HPS-NR3+Cl- to organic / aqueous biphasic catalysts, and realized hydrogenation of alkenes, arenes, ketones, aldehydes, and nitroarenes (M = Pt, Pd, Ru, Rh), oxidation of alcohols (M = Au), and cross-coupling reactions (Pd). R&D groups of Nissan Chemical Co. Ltd. applied M@HPS-NR3+Cl- to electroless plating technology for printing electronics.



Development of reusable iron catalysts for atom transfer radical polymerization.

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Homogeneous catalysis is a powerful tool for synthesizing functional molecules which are applicable to production of pharmaceutical and agricultural chemicals and functional materials for optical and electronic devices and health care. The catalytic species is organometallic molecules, and molecular design of the catalyst resulted in the reactions with high catalytic activity and selectivity. A weak point of molecular catalysis is removal of the metal residues from the product, which are necessary for environmental protection, safety to humans, and production of high material properties but costly. Facile removal of the metal residues is especially important for catalytic production of polymers.

Atom transfer radical polymerization (ATRP) is a reliable method for synthesizing polymers with precise molecular weight and narrow molecular weight distribution. The reaction is initiated by alkyl halides activated by lower valent transition metal compounds (M) to result in generation of alkyl radical species and M-X. The radical species promotes propagation to make polymer chains by contact with vinyl monomers. The radical species at the polymer end is capped by higher valent metal species (M-X). This step is reversible, and control of equilibrium constant, which favors M and polymer-X, actually realizes living polymerization. Many transition metal compounds capable of one electron redox are active towards ATRP, and Cu(I) catalysts are the most famous among them. However, disadvantage of hydrophobic copper catalysts is difficulty in removing the catalyst residue from the polymers produced. Iron is an element which is the most environmentally friendly, abundant transition metal in the earth crust, and inexpensive. A challenging problem is facile removal of the iron residues from the polymers formed. Our discovery is “(TACN)FeX2” species is active catalysts realizing good living nature. Of importance is possible removal of the iron species from the polymer by simple precipitation of the polymer from methanol, and the iron species recovered from the methanol phase is reusable. This unique nature is from equilibrium among monomer, dimer, and trimers of “(TACN)FeX2” shown below. Discussion is focused on how to find the catalyst, catalyst design to improve the catalytic performance, and mechanistic studies.

