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Nanocatalysts: Properties and applications

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Summary

The **first chapter** gives the general background of nanochemistry and optical properties of metal nanoparticles (NPs). This section is divided in three main parts: 1) Metal NPs formation kinetics, their optical properties and different morphologies. 2) Self assembly of NPs in surfactant phases. 3) NPs application in catalysis. In this chapter first we discuss optical properties of metal NPs namely surface plasmon and Mie theory. Then a theoretical approach and detail kinetic model for NPs formation process is discussed. Subsequently our new method for determining the size of metal NPs using their optical properties and their dependence on various parameters of NPs are presented. Various studies for the incorporation of NPs in different surfactant soft assembly are also discussed. In the end we discussed leaching mechanism of Pd NPs catalyzed C-C coupling reaction and different methods for entrapping the homogeneous catalyst.

The **second chapter**, section **A** discusses in detail the nucleation and growth mechanism of Pd NPs in solution. This system has two types of light-absorbing species: Pd ions, that absorb light via electronic transitions, and Pd clusters and aggregates that absorb light via valence–conduction transitions and also scatter light due to their nanometric dimensions. The dynamic changes are monitored by combining *in situ* UV-visible spectroscopy. The reduction and clustering concentration profiles are extracted from the raw data using a combination of net analyte signal (NAS) and principal component analysis (PCA) methods. $PdCl_2$, $Pd(OAc)_2$, and $Pd(NO_3)_2$ are used as Pd^{2+} precursors, and various tetra-*n*-octylammonium carboxylates are applied as reducing and stabilising agents. This *in situ* approach enables the quantification of both the reduction of the Pd^{2+} ions and the growth of the Pd clusters. Kinetic models that account for ion reduction, cluster growth and aggregation are presented and the influence of the counteranions and the reducing agents on these processes is discussed.

In the **section B** the connection between quantum size effects and the surface plasmon resonance of metal nanoclusters is introduced and the pros and cons of *in situ* and *ex situ* cluster analysis methods are outlined. A new method for estimating the size of nanoclusters is presented. This method combines core/shell cluster synthesis, UV-visible spectroscopy and Mie theory. The core/shell approach enables the estimation of metal cluster sizes directly from the UV-visible spectra, even for transition metal nanoclusters like Pd that have no distinct surface-plasmon peak in UV-visible region. Pd/Au and Au/Pd

core/shell clusters as well as Au-Pd alloy clusters are synthesized and used as test cases for simulations and spectroscopic measurements. The results of the simulations and UV-visible spectroscopy experiments are validated using transmission electron microscopy.

In the **third chapter**, we investigated the influence of the reduction state of gold ions on the growth of gold nanocrystals in N,N-dimethyl formamide (DMF). While freshly prepared solutions of $AuCl_3$ produce spherical nanocrystals, aged precursor solutions containing mainly Au^+ ions and Au^0 atoms lead to various branched nanoparticles. Furthermore, we show that also the amount of the reducing and stabilisation agent tetra-n-octylammonium formate (TOAF) plays a decisive role on the shape of the nanocrystals, allowing us to grow triangular and cubic nanoparticles.

Recently the surfactant sponge (L_3) phase is attracting lot of attention in the soft matter world. In the **fourth chapter** we described the preparation of the sponge phase using (SDS/H2O)/ Pentanol/cyclohexane. We doped it with aquasols and organosols of various metal nanoparticles and characterize them using small angle x-ray scattering (SAXS) and optical microscopy. The stability of this phase is then studied against the temperature and external stress. We developed a partial phase diagram of palladium nanoparticle doped sponges.

In the **fifth chapter** the leaching of palladium species from Pd nanoparticles under C–C coupling conditions is proven for both the Heck and the Suzuki reactions using a special membrane reactor. The membrane allows the passage of Pd atoms and ions, but not of species larger than 5 nm. Three possible mechanistic scenarios for palladium leaching are investigated, with the aim of pinpointing the true catalytic species. First, we examine whether Pd° atoms can leach from the clusters under non-oxidising conditions. Using our membrane reactor, we prove that this indeed happens. We then investigate whether small Pd° clusters can in fact be the active catalytic species, by analysing the reaction composition and the Pd species that diffuse through the membrane. Neither TEM nor ICP analysis support this scenario. Finally, we test whether Pd^{II} ions can leach in the presence of PhI *via* oxidative addition and formation of $Ar–Pd^{II}–I$ complexes. Using mass spectrometry, UV-visible spectroscopy and ^{13}C NMR spectroscopy, we observe and monitor the formation and diffusion of these complexes, showing that the first and the third options are both possible, and indeed are likely to occur simultaneously. Based on these findings, we maintain that Pd nanoparticles are not the true catalysts in C–C coupling. Instead, catalysis is carried out by either Pd° atoms and/or Pd^{II} ions that leach into solution.

The **sixth chapter** presents a simple and practical concept and device for homogeneous catalyst separation. The device is a two-layered ceramic membrane cylinder that allows the diffusion of reactant and product molecules in and out, but keeps the catalyst trapped inside. The concept is demonstrated for the enantioselective transfer hydrogenation of acetophenone to *(s)*-phenethyl alcohol, using large molecular catalysts, that are anchored on Fréchet-type dendrimers. The robustness, low cost, and high precision features of the ceramic membranes make them ideal for such practical applications.