Van Leeuwen Research Group

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Abstract

In 2013 the main activity of the group has been the synthesis, identification and catalysis studies of ligand modified metal nanoparticles (MNPs), a study conducted in collaboration with the group Chaudret/Philippot in Toulouse. The focus was on small MNPs modified by phosphine ligands with the aim to develop ligand effects similar to those that have been used extensively in homogeneous catalysis of discrete metal complexes. Several metals were studied and particularly ruthenium showed a clear ligand effect; the stronger the donor, the more active is ruthenium as an arene hydrogenation catalyst. The stability decreases simultaneously and the most productive catalysts are based on dicyclohexyl aryl phosphine. Application of MNP catalysts most likely requires their immobilization on solid supports to enable separation and for that reason several immobilization studies have been undertaken. While for metal complexes the catalytic activity decreases when they are immobilized, for RuNPs we found that the activity increases with an order of magnitude, most likely because the stability is enhanced. Secondary phosphine oxides (SPO) led to lower activities for all hydrogenation reactions using Ru and in this case the generally expected "poisoning" of the heterogeneous catalyst by ligands occurs. For gold-SPO NPs on the contrary we found a highly selective activity for aldehyde hydrogenation while other functional groups were not affected. As a mechanism we proposed a heterolytic cleavage of dihydrogen by a pair of Au-O atoms.

Ligand effects in MNP catalysis

The main variable for heterogeneous transition metal catalysts is the solid used as a support for them to enable a practical use of the metal particles. The supports used vary enormously and they have increased in number in the last decades considerably. We mention as examples a wide variety of oxides, sulfides, nitrides, and silicon, many forms of carbon, metal-organic frameworks, resins, polymers, etc. These extensive studies were undertaken because the support has considerable influence on the properties of the metal as a catalyst. The effect of ligands coordinated to the metal surface, however, has been much less studied as in general ligands such as carbon monoxide, phosphines, thiolates etc were found to be poisons for the catalytic activity. There are several exceptions and carbon monoxide in some cases may enhance the rate of reaction although it is not a reactant (e.g. in oxidation reactions with gold catalysts), and a few chiral modifiers have been discovered that induce enantioselectivity in hydrogenation reactions of a limited number of substrates (cinchona molecules on Pt and tartaric acid on Ni).

In the last 15 years Metal Nano Particles (MNPs) have become subject of numerous studies; metal particles of sizes ranging from 1–10 nm have a much larger fraction of surface atoms than the metal particles on support used commercially. In large clusters of sizes 1–2 nm more than half of the metal atoms are located at the surface. Thus, potentially in these MNPs the catalytic activity can be much higher per total material than in particles >10 nm.

Thermodynamically small MNPs are less stable than bulk metal and there is a thermodynamic driving force to form larger particles. During the synthesis of MNPs therefore they must be stabilized to prevent agglomeration or further growth, called Ostwald ripening in this instance. Such stabilizers can be detergents, polymers, salts, dendrimers, and weakly or strongly binding ligands, such as alcohols, amines, phosphines, thiolates, etc. Mechanistically the formation by reduction of metal salts may take place inside micelles and the ligands forming the micelles of the polymers wrapped around them inhibit coagulation. Amine based dendrimers were shown to give MNPs containing as many metal atoms as were present in the polymetal complex of the starting dendrimer.

Especially the organometallic synthetic methods can lead to phosphine stabilized MNPs and it has been found by several authors and ourselves that the ligands may exert an influence on the catalytic properties as they do in well defined monometallic or bimetallic organometallic catalysts. A second goal of our work was the use of oligodentate phosphorus ligands that by the nature of their backbone are not suited for the formation of organometallic species, but which can accommodate easily metal nanoparticles. Two examples of such ligands are shown in Figure 1 together with two ligands leading to unusual organometallic complexes, Xantphos and Methanodioxocin-diphos.
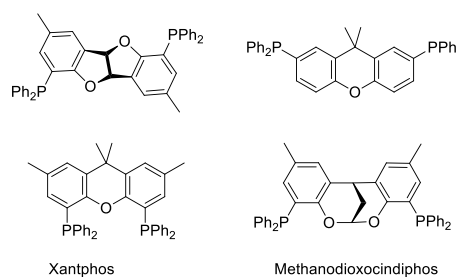

Fig. 1 – *Ligands suited for MNPs but not for routine organometallic complexes (top).*

In a collaboration with the groups of Philippot and Chaudret in Toulouse a wide variety of such ligands were used in the synthesis of RuNPs from an organometallic precursor (cod)(cot)Ru in the presence of hydrogen. As was known for this method, in all cases RuNPs were obtained, the size of which depended on the conditions and the ligand used. In several cases partial or complete hydrogenation of the phenyl groups and even the aromatic backbone was observed when this method was used. The method is reproducible and the cyclohexyl derivatives of the ligands when used from the start gave the same products as the phenyl ligands that underwent *in situ* hydrogenation to the cyclohexyl groups.

Compared to organometallic chemistry full identification is a tedious process and even after having applied all available techniques (TEM, HRTE, EDX, Uv-vis, DLS, elemental analysis, MS, MAS NMR, HR MAS NMR, TGA, *etc.*) there remain still questions as to the structure, surface and composition of the products. One general finding of this method for Ru, regarded as the cleanest method compared to other ones, such as borohydride reduction of halide salts, is that it

proceeded best in tetrahydrofuran. This solvent however was decomposed by Ru and H_2 and gave a hydrocarbon polymer and water. The nanoparticles are imbedded and stabilized in this polymer matrix, it is thought, which is also evidenced by the inability to obtain DLS data for these nanoparticles. Ru metal content is around 30%, the sizes vary between 1 and 3 nm and a RuNP of 50 atoms, 1.1 nm, contains about 8 P atoms, which represents a high surface coverage.

The RuNPs were all applied in the RuNP@ligand catalyzed hydrogenation of aromatics and substituted aromatics containing additional groups that can undergo hydrogenation such as alkenes, alkynes, nitro and keto groups. The RuNPs prepared this way are extremely active catalysts for hydrogenation and in addition to the hydrogenation of the aromatic rings most functionalities are hydrogenated as well and selectivities are in general low. For the hydrogenation of aromatics a distinct ligand effect was observed; stronger donor ligands give a higher initial rate of hydrogenation (NHC > trialkylphosphines > dialkylarylphosphines > triarylphosphines). The stability of the catalyst follows the same order and the highest turnovers were obtained with dicyclohexyl arylphosphines. Immobilization of the RuNPs on solid supports (silica, alumina, carbon) led to an increase of the activity and turnover number, which should probably be ascribed to their higher stability of the supported catalysts. An immobilized homogeneous catalyst usually shows much lower activity than its homogeneous analog. For practical application of MNPs as catalysts such immobilization would be necessary to enable separation of product and catalyst.

Secondary phosphine oxides (SPO) are being studied as ligands for MNPs since it is thought that their metal complexes will possess the ability to cleave H_2 heterolytically (Fig. 2) across M and O and, subsequently, transfer both hydrogen atoms to a suitable substrate, similar to what we have shown for molecular catalysts.
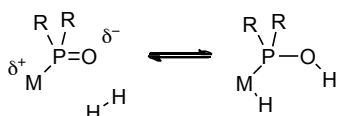

Fig. 2. *Heterolytic cleavage of dihydrogen*

For RuNPs the use of SPOs led to a sharp decrease of hydrogenation activity, which one could describe as the generally expected effect of ligands added to an active solid catalyst. Since SPOs were thought to enhance heterolytic cleavage, the selectivity for acetophenone hydrogenation was studied and indeed a shift towards ketone hydrogenation was found, but selectivities remained moderate, for both phosphine and SPO ligated RuNPs.
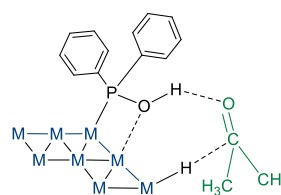

Fig. 3. *Heterolytic dihydrogen transfer*

Subsequently we focused on Group 11 metals (Cu, Ag, Au) for SPOs as it is known that MNPs and large clusters of these metals always contain anionic ligands on the surface, thiolates being the most often used counteranion. In the absence of thiolates, reduction of the large cluster is often incomplete as shown by phosphine stabilized Au clusters that usually contain halide anions.

For several SPOs we obtained AuNPs with a narrow particle distribution (1.3 nm) and an average composition of $Au_{50}SPO_{30}$. The particles were fully characterized and the SPOs are present as the anions on the surface as shown in Figure 4, whereas in organometallic complexes SPOs always form bidentate monoanions as shown on the left, but for such pairs there would be no space on the surface in high numbers. Also for 30 SPO anions we have calculated that surface coverage is complete and very dense. The composition strongly resembles that of thiolate ligated AuNPs, which have been extensively studied in the last two decades.
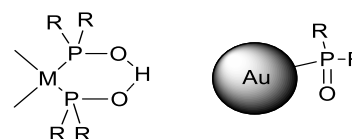

Fig. 4. *Binding mode of SPOs in organometallic complexes (left) and on AuNPs*

Gold is not a common metal for hydrogenation reactions, but AuNP@SPO are active catalysts for aldehyde hydrogenation. It was found that a selective hydrogenation of aldehydes can be achieved in the presence of ketones, alkenes, nitro groups *etc* and even acrolein can be hydrogenated to allyl alcohol > 99% selectivity, a feature never observed with heterogeneous catalysts.
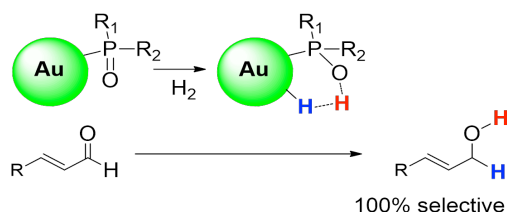

100% selective

Fig. 5. *Heterolytic mechanism for aldehyde hydrogenation with AuNP@SPO*

Only terminal alkynes interfere as they partially replace the SPO ligands forming stable alkynyl groups on the surface. Further evidence for H_2 activation was found by te formation of DH when the catalyst was subjected to a mixture of D_2 and H_2. In the absence of SPO neither Au metal nor its complexes show hydrogenation of aldehydes or HD formation. The synthesis of resorcinarenes as templates (Figure 6) for MNPs was continued and a variety of tetraphosphines was synthesized. MNPs of group 11 metals have been prepared successfully. As mentioned above, both thiolates and phosphines have been reported as ligands for clusters and NMPs of Group 11 metals, but a combination thereof is lacking; thiolates provide the stabilizing anion required and phosphines can be used for electronic and steric modification. The simplest phosphinothiol is shown in Figure 5, which for Cu gave a mixture of CuNPs and clusters from which a Cu_{18} cluster was isolated and identified by X-ray crystallography. It contains 10 anionic phosphinothiolate ligands and a number of hydrides as hydrogen can be liberated by several reactions.
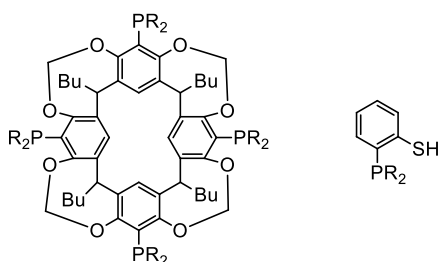

Fig. 6. *New ligands for Group 11 MNPs*

Homogeneous catalysis

Rhodium catalyzed hydroformylation of olefins is a well-studied homogeneous catalytic reaction and high selectivities to linear products can be obtained with several catalyst systems. In recent years also a number of catalysts were reported that give high enantioselectivities for monosubstituted and 1,2-disubstituted alkenes. However, the development of efficient and selective catalytic systems for 1,1- disubstituted has proven to be a formidable challenge in terms of activity and enantioselectivity.

The high π-acidity of pyrrolyl phosphoramidites was disclosed as a highly desirable attribute for hydroformylation of octane at very high rates and with a very high preference for terminal functionalization. We therefore thought that amidites of this type combined with chiral bisphenol derivatives would be good candidates for the asymmetric hydroformylation of 1,1-substituted alkenes. A variety of such ligands has been made. All of them give moderate to excellent conversions with high regioselectivity but enantioselectivities of only 50% or less.
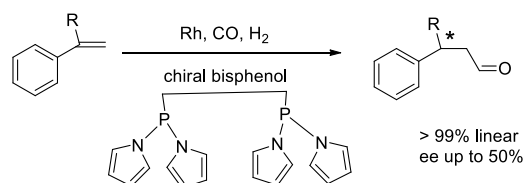

> 99% linear
ee up to 50%

Fig. 7. *Asymmetric hydroformylation of 1,1-substituted alkenes*

The work on remote chiral control in supramolecular catalysts based on Ti, ditopic heterobidentate ligands made from Schiff-base/phosphine and Schiff-base/pyridine ligands, and chiral diols (Fig. 8) was continued with the asymmetric hydrogenation of substituted alkene without further functionalities. The so-called Phox ligands which are used for this type of reaction are unique, it was thought, but much to our surprise the present supramolecular catalysts gave enantioselectivities up to 90%.
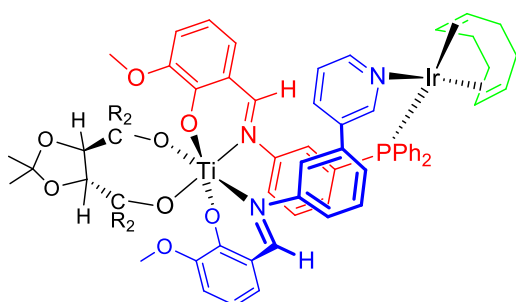
Fig. 8. *Supramolecular, asymmetric catalyst for alkene hydrogenation*

Articles

"Strong π-acceptor ligands in rhodium-catalyzed hydroformylation of ethene and 1-octene: Operando catalysis"
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J. Rich, M. Rodríguez, I. Romero, X. Fontrodona, P. W. N. M. van Leeuwen, Z. Freixa, X. Sala, A. Poater, M. Solà