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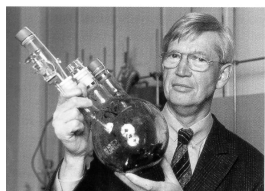
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Nanostructured Transition Metals

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1.   A Brief Introduction

Nanoparticulate transition metals are generally defined as isolable particles between l and 50 nm in size. As it is obvious from Fig. 1., the main interest for potential applications of these materials stems from their huge surface areas. It has been calculated that *e.g.* an iron cube of 10nm size exhibits 10% of the atoms at the surface whereas downsizing these particles to 2.5nm exposes 60% of the atoms at the surface [1].
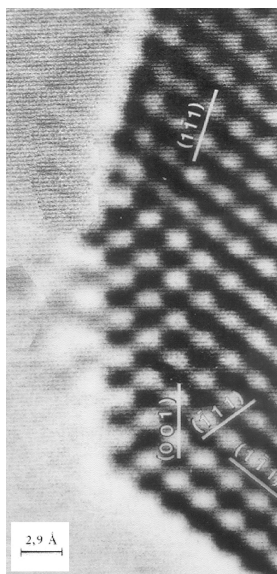
**Fig. 1: Nanoparticulate Platinum
in High Resolution Transmission Electron Microscopy**

This article will cover the following scope of subjects: Metal Nanopowders, Metal Nanoparticles, Nanoparticulate Metal Colloids, Magnetic Fluids, Metallic Nanoclusters, and Heterogeneous Nanocatalysts.

Nanoparticulate transition metal materials can be obtained in the form of **metal nanopowders**, where the grain size ranges between 5 – 50 nm and **metal nanoparticles** of 1 – 10 nm size having a relatively narrow size distribution. Nanoparticulate **metal colloids** are isolable particles with sizes between l and 15nm where the metal cores are prevented from agglomeration by colloidal protecting shells. Metal colloids can be redispersed in organic solvents **("organosols")** or water **("hydrosols")**. A special form of colloidal metals are **magnetic fluids** where magnetic metal particle cores such as Fe, Fe/Co alloys or Co are covered by mono- or bilayers of special peptisation agents to give stable dispersions ("fluids") in a variety of organic media (*e.g.* kerosene, silicon oil) or water. In contrast to nanoparticles which are characterized only by their size and elemental composition, metallic **nanoclusters** contain a defined number of metal atoms, *e.g.* Ti_{13} or Au_{55}. In a number of cases nanoclusters can even be described as normal chemical compounds having defined chemical formulae such as [Ti_{13} x 6THF] [2] or $Au_{55}(PPh_3)_{12}Cl_6$ [3].

Nanostructured metal particles have been obtained either by so called "top down methods", *i.e.* by the mechanical grinding of bulk metals, or via "bottom-up methods" which rely on the wet chemical reduction of metal salts or, alternatively, the controlled decomposition of metastable organometallic compounds such as metal carbonyls. For the production of nanoparticulate metal colloids a large variety of stabilizers, e.g. donor ligands, polymers, and surfactants, are used to control the growth of the initially formed nanoclusters and to prevent them from agglomeration. The chemical reduction of transition metal salts in the presence of stabilizing agents to generate zerovalent metal colloids in aqueous or organic media was first published in 1857 by M. Faraday [4] and this approach has become one of the most common and powerful synthetic methods in this field [5 – 7]. The first reproducible standard protocols for the preparation of metal colloids (*e.g.* for 20nm gold by reduction with sodium citrate) were established by J. Turkevich [8 – 10]. He also proposed a mechanism for the stepwise formation of nanoparticles based on nucleation, growth, and agglomeration, which in essence is still valid. Data from modern analytical techniques and more recent thermodynamic and kinetic results have been used to refine this model as illustrated in Fig. 2.
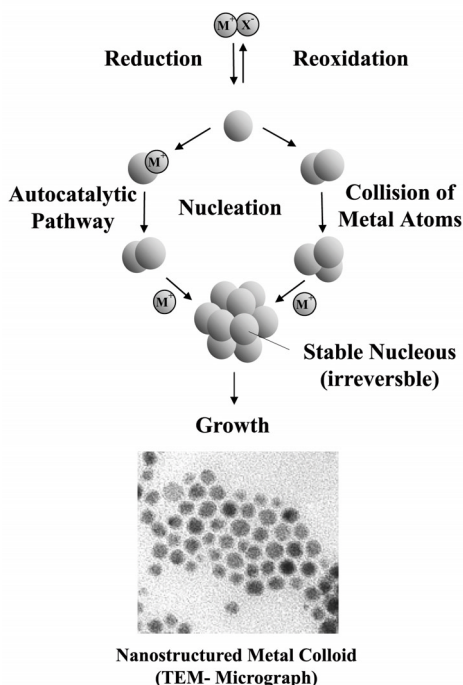
**Fig. 2: Formation of nanostructured metal colloids
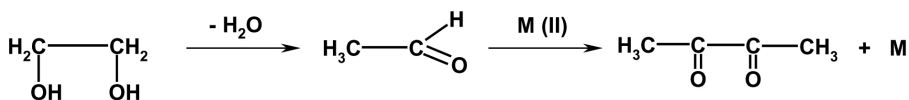by the "salt reduction method"**

In the embryonic stage of the nucleation, the metal salt is reduced to give zerovalent metal atoms. These can collide in solution with further metal ions, metal atoms, or clusters to form an irreversible "seed" of stable metal nuclei. The diameter of the "seed" nuclei can be well below l nm depending on the strength of the metal-metal bonds and the difference between the redox potentials of the metal salt and the reducing agent applied. The formation of nanoparticulate metal colloids via "reductive stabilisation" using organo aluminum reagents follows a different mechanism which has been recently elucidated in detail [11].

During the last few decades a considerable body of knowledge has been accumulated on these materials (see the reading list). Highly dispersed mono- and bimetallic colloids can be used as precursors for a new type of catalyst that is applicable both in the homogeneous and heterogeneous phases [12]. Besides the obvious applications in powder technology, material science and chemical catalysis, recent studies have examined the great potential of nanostructured metal colloids as advantageous fuel cell catalysts [13].

2. Metal Nanopowders

Nanostructured metal and alloy powders may be produced either via the reduction or co-reduction of metal salts using alkaline-triorganohydroborates [6] or using the "polyol"- [14 – 16] or the "alcohol-reduction" [17 – 19] pathways.

The triorganohydroborate reduction of *e.g.* Pt-salts yields Pt nanopowders of ca. 3 – 4nm size with purities of > 95% . The size distribution, however, is relatively broad and the product is contaminated with small residues of alkaline halides. Via the Polyol Method (see equation below) relatively large Pt nanopowders (*e.g.* 5 – 13nm) are obtained in > 99% purity. The reduction is based on the decomposition of the ethylene glycol and its conversion to diacetyl.

$$H_2C(OH)-CH_2(OH) \xrightarrow{- H_2O} H_3C-C\overset{H}{\underset{O}{<}} \xrightarrow{M (II)} H_3C-\overset{O}{\underset{||}{C}}-\overset{O}{\underset{||}{C}}-CH_3 \; + \; M$$

N. Toshima from the Science University of Tokyo in Yamaguchi has introduced the alcohol reduction method in the field of nanopowder synthesis [17 – 19]. Alcohols such as methanol, ethanol or propanol work simultaneously as solvents and as reducing agents, being oxidized to aldehydes or ketones. Refluxing metal salts or complexes (such as H_2PtCl_6, $HAuCl_4$, $PdCl_2$, $RhCl_3$ in an alcohol/water solution (1/1, v/v) yields nanocrystalline metal powders in the absence of stabilizers. In the case of Pt, the alcohol reduction of H_2PtCl_6 gives $Pt^{(0)}$ particles of ≈ 3nm size, however with a broad size distribution, and moderate purity (80 – 90%). It should be mentioned here that in the presence of protective polymers such as polyvinylpyrrolidone (PVP), homogeneous colloidal dispersions, *e.g.* nanometal Pt colloids of 2.7nm size are obtained.

Metal nanopowders are of considerable interest in industrial powder technology, metallurgy [20], and in catalysis [21].

3. Metal Nanoparticles

In contrast to Metal Nanopowders which tend to agglomerate to larger grains and where Electron Microscopy shows large particle sizes with a relatively broad size distribution, "Metal Nanoparticles" generally exhibit small sizes, well defined and regular shapes and have histograms with a narrow size distribution curve (i.e. a good "monodispersity"). In case of Platinum, spherical nanoparticles of 4nm ± 0.5nm size are available from pre-prepared 4nm Pt-NR_4Cl Organosols (see below) by removing the colloidal stabilizer (i.e. the NR_4Cl) from the particle surface via repeated washing [6, 22]. Recently, a novel, size-selective preparation route was found for the manufacture of air stable "monodispersed" colloidal cobalt nanoparticles via the thermolysis of $Co_2(CO)_8$ in the presence of aluminum alkyls [23]. X-ray absorption near edge structure measurements have proven that subsequent "smooth air-oxidation" provides long term air-stable zerovalent magnetic cobalt particles of *c.a.* 10nm ± 0.5nm size (see Fig. 3). A similar procedure leads to zerovalent, air-stable nanoparticles of Ni, Fe, and to Fe/Co alloys.
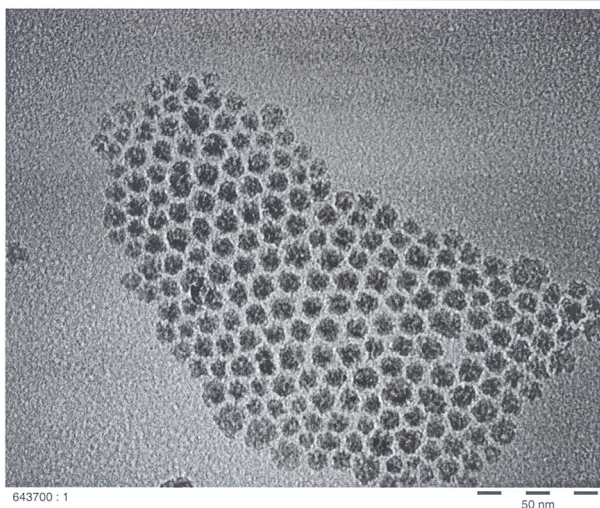
Fig. 3: TEM micrograph of air-stable 10 nm cobalt particles

Some interesting applications of these materials may soon develop in metallurgy and special fields of powder technology. In wet form these monodisperse Fe-, Co-, Ni- and Fe/Co alloy particles may be transformed into powerful magnetic fluids (see below).

4. Nanoparticulate Metal Colloids

4.1 Organosols

The reduction of metal salts using tetraalkylammonium-hydrotriorganoborates in organic solvents yields metal colloids stabilized by NR_4^+. The metal particles are well protected by long chain alkyl groups, which make the colloid very soluble in lipophilic organic phases giving up to one molar solutions of zerovalent metals:

$$MX_v + v\,NR_4(BEt_3H) \longrightarrow M_{colloid} + v\,NR_4X + v\,BEt_3 + v/2\,H_2$$

M = metals of the Group 6 – 11 of the Periodic Table; X = Cl, Br;

v = 1, 2, 3; R = alkyl, $C_6 - C_{20}$

This very versatile classic method [24] yields generally monodisperse nanoparticulate organosols of 2 – 3nm size, *e.g.* Cr (2 – 3nm), Mo (2.5nm), Fe (3nm), Co (2.8nm), Ni (2.8nm), Rh (2.1nm), Pd (2.5nm), and Pt (2.8nm). Relatively small particles are found in case of Ru (1.3nm) and Ir (1.5nm). In the coin metal series larger

particle sizes are produced with this procedure, *e.g.* Cu (8.3nm), Ag (8 – 13nm), and Au (10nm). Typically the organosols are isolated as viscous, waxy materials which contain ca. 4 – 10 wt-% of metal. The protecting shell can, however, be washed away to increase the metal content of the sol. For example, a raw Pt organosol containing 4 – 6 wt.-% of Pt can be "purified" by redispersion in ether and subsequent precipitation with ethanol. After drying a greyish-black Nano-Pt-colloid is obtained (size: 2.8nm ± 0.5nm) which contains 70 – 90 wt.-% of Pt depending on the degree of washing. Similarly, a N(Octyl)$_4$Cl-stabilised rhodium organosol (size: 2.1nm ± 0.5nm) may be "purified" to give a greyish-black nano-Rh-colloid containing 73 wt.-% of Rh. Via co-reduction of the corresponding metal salts, a 1.7nm ± 0.5nm bimetallic N(Octyl)$_4$Cl-stabilised Pt/Ru colloid (6.9 wt.-% Pt; 3.6 wt.-% Ru) is formed which serves as a valuable precursor to fuel cell anode catalysts [25, 26]. A small sized N(Octyl)$_4$Br-stabilised gold colloid (2.6nm ± 1.1nm) is available from the thermal decomposition of HAu(NO$_3$)$_4$ x 3 H$_2$O in the presence of N(Octyl)$_4$Br. This material is a good precursor to nanostructured gold and alloy catalysts [27] and electrocatalysts [28]. The controlled decomposition of low valent complexes, preferably in the presence of stabilizers, yields very clean nanoparticulate precursors for fuel cell catalysts and may be applied also for the decoration or coating of preformed metal cores [29]. It is, however, restricted to the availability of appropriate "starting complexes   (see Fig. 4).
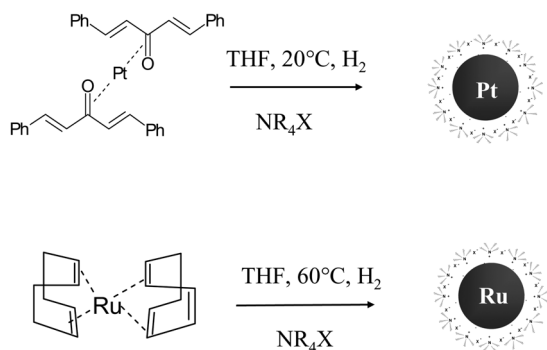

**Fig. 4: Organosols via hydrogenolysis and thermolysis
of organometallic complexes**

A special case of organosol preparation via controlled complex decomposition is the recently found decomposition of (CH$_3$)$_2$PtCOD in the presence of trialkylaluminum [30]. As shown in Fig. 5, extremely small Pt particles (size 0.8nm) are formed which represent the first "full shell cluster" of Pt having 13 Pt atoms. Remarkably, the protecting shell of these organosol type consists exclusively of alkylaluminum which can be easily removed by washing. On the exposure to air the alkylaluminum shell is oxidized to give a Al$_2$O$_3$ matrix where the small Pt particles are regularly distributed as shown in the High Resolution TEM Micrograph (Fig. 5).

$$(CH_3)_2PtCOD + nAl(C_2H_5)_3 \longrightarrow$$

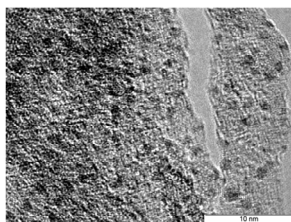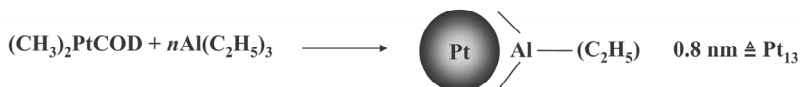Pt   Al——(C$_2$H$_5$)   0.8 nm ≙ Pt$_{13}$

Fig. 5: Formation of 0.8nm Pt stabilized by trialkylaluminum

Organoaluminum compounds have been used for the "reductive stabilization" of mono- and bimetallic nanoparticles [7, 11] to give organometallic organosols as shown in Fig. 6.
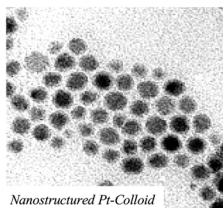

$$MX_n + AlR_3 \xrightarrow{\text{Toluene}} M_{colloid} + [R_2Alacac]$$

M = Metals of Groups VIA-VIIIA und IB PSE
X = Halogen, Acetylacetonate
n = 2-4
R = C$_1$-C$_8$-Alkyl

Nanostructured Pt-Colloid

Pt-colloid from Ptacac$_2$ and Al(Methyl)$_3$ (1-2nm)
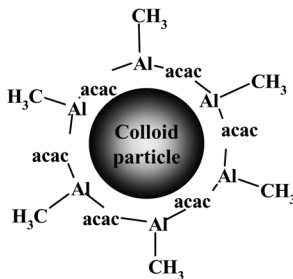
**Fig. 6: Reductive stabilization of organosols (*e.g.* 1 – 2 nm Pt)
with trialkylaluminum**

According to Fig. 6, colloids of zerovalent elements of Groups 6 – 11 of the Periodic Table, and also of tin, may be prepared in the form of stable, isolable organosols. Available analytical data suggest that a layer of condensed organoaluminum species protects the transition metal core against aggregation, as depicted in Fig. 6. However, the exact "backbone" of the colloidal organoaluminum protecting agent has not yet been completely established.

Unreacted organoaluminum groups (e.g. A1-CH$_3$, Al-C$_2$H$_5$) from the starting material are still present in the stabilizer and have been detected by quantitative protonolysis experiments.

4.2 Hydrosols via "Reductive Stabilisation" and subsequent "Modification"

The active Al-C bonds have been used for a controlled protonolysis by long-chain alcohols or organic acids ("modifiers") to give Al-alkoxide groups in the stabilizer (Fig. 7).

Modification

Organosol + Modifier = Modified Sol

Modifiers: e.g. alcohols, carbonic acids, silanols, sugars,
          polyalcohols, polyvinylpyrrolidone,
          surfactants,
          silica, alumina, etc.
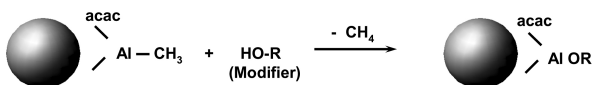
Advantages: Tailoring of the dispersion in lipophilic and/or hydrophilic solvents
(e.g. water) Anchoring onto surfaces via d-bonds

Fig. 7: Hydrosols via modification of the Al-organic protective shell

This "modification" (Fig. 7) of the organoaluminum protecting shell can be used to tailor the dispersion characteristics of the original organosols. A vast spectrum of solubilities of the colloidal metals in hydrophilic media (including water) has been achieved in this way. Inorganic surfaces bearing OH groups can react with the active Al-C bonds in the colloidal protecting shell, opening new possibilities for the preparation of heterogeneous catalysts. The modification process does not substantially alter the particle size of the metal core (Fig. 8).

Example:

Pt/Ru-Organosol + Modifier $\Rightarrow$ Pt/Ru-Hydrosol

Modifier: Polyethylene glycol dodecyl ether (*Brij 35* ®)
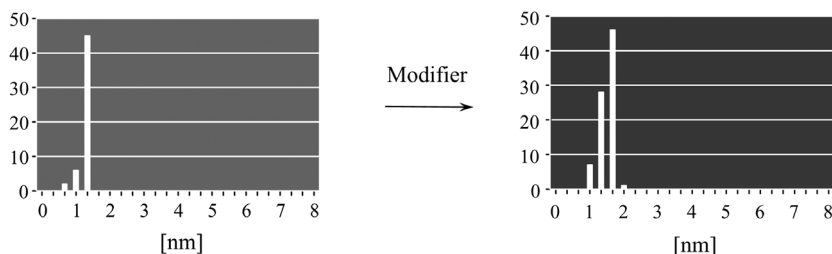
Modifier

Good solubility: >100mg/At metal in aromatics, hydrocarbons, ethers, alcohols, ketones, and water

Fig. 8: Size conservation of colloidal Pt/Ru particles under the hydrophilic modification of the $(CH_3)_2Al$-acac protecting shell using polyethylene glycol/dodecyl ether

Hydrosols are also available through the Polyol- [14 – 16] or the Alcohol Reduction Method [17 – 19] as mentioned above.

5. Magnetic Fluids

Magnetic fluids (MFs) with narrow size distributions exhibit useful properties for a number of technical and biomedical applications. The magnetic properties of MFs depend strongly on the size of the particles and the concentration of the magnetic material in dispersion. The well known magnetite MFs have a good stability. However, the magnetic properties of these materials are not sufficient for a number of purposes. Consequently, stable MFs on the basis of nanosized metallic Fe-, Co- or Fe/Co alloy colloids are very interesting materials. Air-stable, colloidal, metallic particles (Fe, Co, Ni, and Fe/Co) with a narrow size distribution are accessible via the thermolysis of metal carbonyls in the presence of aluminum alkyls. Subsequent "Smooth Air Oxidation" leads to long term stable metallic magnetic nanoparticles, as was evidenced by XANES and other physical methods [23, 31, 32].

The isolated particles can be dried for powders or peptised with the help of surfactants resulting in remarkably stable metallic magnetic fluids (MF) applicable for a number of practical purposes. The influence of the aluminum alkyls during the decomposition of $Co_2(CO)_8$ in toluene was studied by IR spectroscopy. It was found that the aluminum alkyls act as catalysts for the thermal decomposition of the metal carbonyl via $Co_4(CO)_{12}$ and higher Co carbonyls to give "monodisperse" Co nanoparticles.

Via peptisation of the obtained metallic or bimetallic magnetic nanoparticles, magnetic fluids in different carrier liquids, such as water, hydrocarbons, kerosene, mineral and

vacuum oils, and silicones, are obtained by using suitable surfactants for each carrier liquid. Suitable surfactants combine strong adsorption properties on the particle surface, good protecting abilities to prevent the particles from oxidation, and good solubility in carrier liquids. The optimal quantity of the surfactants and the best conditions of stabilization have to be elaborated individually.

Water based magnetic fluids are also accessible via mono-, bi- or polylayers formed around the particles when ionic, non-ionic, or double surfactants are applied. These air stable magnetic fluids have a high potential for a number of technical and biomedical applications. The magnetic fluids were investigated for their magnetic properties by TEM (Transmission Electron Microscopy), by Moessbauer spectroscopy, by DRIFTS (Diffuse Reflection Infrared Fourier Transform Spectroscoy), UPS (Ultraviolet Photoelectron Spectroscopy), and MIES (Metastable Impact Electron Spectroscopy). The resulting magnetic fluids exhibit extraordinary magnetic properties at low concentrations of the magnetic material (see Fig. 9) and show unusual high magneto-viscous effects.
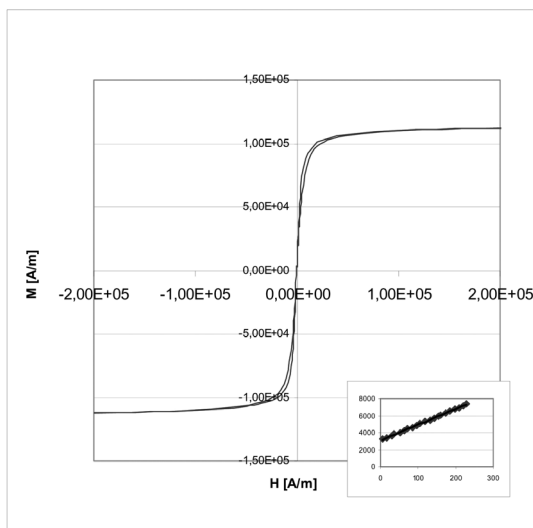
Fig. 9: **High saturation magnetisation (120.1 kA/m = 151mT = 1510G)**
of a 8.21 Vol-% Co-Kerosene fluid (particle size 11nm)

By TEM it was confirmed that the particle size was not altered during the peptisation process. Moessbauer investigations of Fe and Fe/Co magnetic fluids in kerosene revealed that the particles consist of a metallic or bimetallic core which is protected against air-oxidation by a shell of Fe^{3+} ions (probably Fe carboxylates and/or Fe oxides). The resulting Moessbauer spectra show a superimposition of the spectra of Fe or the Fe/Co alloy (major component) and Fe^{3+} as the minor component. In the case of the Co(0) fluid, according to DRIFTS, UPS, and MIES, the anticorrosive shell consists of Co carboxylates and Co oxides.

6. Metallic Nanoclusters

The regular Ti_{13} cluster of the formula [Ti_{13} x 6 THF] stands at the very beginning of the row of the so-called full shell clusters. The metal nuclei consist of a number of atoms that follow hexagonal or cubic close packing. The THF ligands were found via XANES / EXAFS techniques to form an octylahedral configuration [2] (Fig. 10).
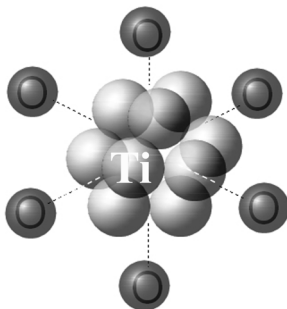

**Fig. 10: A regular $Ti^{(0)}_{13}$ cluster having 6 THF-O atoms
in an octahedral configuration**

Since no particles are detectable in TEM, the size of the cluster must be <0.8nm. XPS/XANES have revealed that Ti is present in metallic form. EXAFS shows signals at 1.6 Å and 2.4 Å, but no signals from backscatterers >3 Å which confirms the small size of the Ti cluster. Ti-Ti distances were found to be 2.804 Å and the Ti-O distance is 1.964 Å. The elemental analysis of the as prepared Ti_{13}-THF cluster samples show ca. 20 wt-% of metal indicating some residues of KBr resulting from the metathesis reaction of $TiBr_4$ x 2 THF and $K[B(ethyl)_3]H$. Via further purification, the Ti content can be increased up to 43.5% Ti indicating a very low KBr contamination of ca. 1 wt.-%. The Ti_{13}-THF cluster has been found to be one of the best catalysts available for the reversible hydrogen storage in alanates [33, 34]. For this purpose it can be used regardless of the KBr content without further purification. Also, it is a good catalyst for the hydrogenation of Ti- and Zr- sponges and has been used as a powerful activator for heterogeneous noble metal hydrogenation catalysis [6, 7].

The two-shell Au_{55} core of G. Schmid's $Au_{55}(PPh_3)_{12}Cl_6$ nanocluster exhibits the same cubic close-packed (ccp) structure as is found in bulk gold [3]. $Au_{55}(PPh_3)_{12}Cl_6$ is probably the most frequently investigated full-shell cluster. Since its size definitely represents the transition from bulk to molecule, this cluster is regarded as the prototype of quantum dots [36]. Numerous derivatives of the PPh_3-stabilized Au_{55} cluster are available by ligand exchange reactions [37]. $Ph_2PC_6H_4SO_3Na$ removes PPh_3 quantitatively from $Au_{55}(PPh_3)_{12}Cl_6$ to yield a completely water soluble compound [38]. Further, the formation of two- and three- dimensionally organized ligand-protected Au_{55} has been described [39]. Techniques for the generation of ordered monolayers and artificial patterns of quantum dots are currently developed. The expanding role of gold nanoclusters in inorganic biochemistry has been shown e.g. in the recently reported formation of nanowires via the combination of 8Å-DNA-

sequences with Au$_{13}$ clusters yielded during the interaction of Au$_{55}$[P(C$_6$H$_5$)$_3$]$_{12}$Cl$_6$ with DNA via the degradation. These systems are regarded as promising for tumor treatment [40].

7. Heterogeneous Nanocatalysts [12]

In catalysis, nanostructured metal colloids are often considered as "dissolved surfaces" having highly unsaturated atoms. The incentives for the application of these materials as precursors for the manufacture of metal-colloid catalysts [22] emerge from the enhanced activity, good selectivity (controllable via the colloidal modifiers), synergistic effects in bimetallic particles, and a remarkable long-time stability. An additional potential for catalytic applications exists when these colloidal metals are dispersed in zeolites, mesoporous environments, micelles, and biomembranes.

Another field of application for these colloidal metals is electrocatalysis applied to fuel cells. From recent papers on fuel cell technology [13] it may be deduced that the commercialization of CO-tolerant, high-performance electrocatalysts based on colloidal bimetallic particles, sized below 2nm, may be significantly accelerated especially in the automotive sector.

A great deal of industrial interest has been attracted by the potential for the manufacture of heterogeneous catalysts using pre-prepared nanometal colloids as precursors using the so-called "precursor concept" [22]. An obvious advantage of the new preparation mode compared with the conventional salt-impregnation method is that both the size and the composition of the colloidal metal precursors may be tailored for special applications independently of the support. In addition, the metal particle surface may be modified by lipophilic or hydrophilic protective shells, and covered by intermediate layers, e.g., of oxide. The addition of dopants to the precursor is also possible. The second step of the catalyst manufacture consists of the simple adsorption of the pre-prepared particles by dipping the supports into organic or aqueous precursor solutions at ambient temperature. This was demonstrated, e.g., for charcoal, various oxidic support materials, and even low-surface materials such as quartz, sapphire, and highly oriented pyrolitic graphite (HOPG). A subsequent calcination step is not required (see Fig. 11).
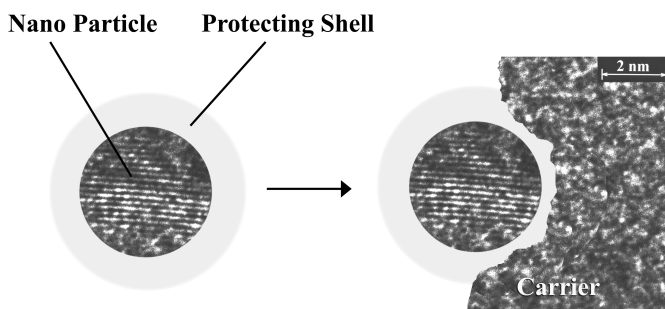

Fig. 11: The precursor concept

7.1 Hydrogenation

In the butyronitrile hydrogenation standard test [41], the activity of surfactant-stabilized colloidal rhodium (5 wt-% on charcoal) was found to surpass that of conventional salt impregnation catalysts of the same metal loading. The addition of 0.2 wt-% of the Ti_{13} cluster (Fig. 10) to the carbon-supported Rh colloid as a dopant resulted again in a significant enhancement of the hydrogenation activity.

An example of the application of supported, nanostructured metal colloids in fine chemical catalysis is the cis-selective partial hydrogenation of 3-hexyn-l-ol to give leaf alcohol, a valuable fragrance, produced in 1996 to the amount of 400 t including esters (see Figure 12) [42, 43].
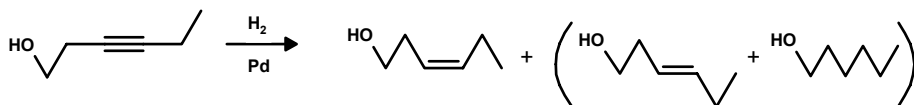

Fig. 12: Regioselective hydrogenation

The performance of heterogeneous catalysts based on surfactant-stabilized palladium colloids was compared with conventional Pd/C and Lindlar catalysts in the partial hydrogenation of 3-hexyn-l-ol under optimized reaction conditions. It was found that the selectivity can be influenced by the protective shell as well as by the support and various promoters. The zwitterionic surfactant sulfobetaine-12 (N,N-dimethyldodecylammoniopropane sulfonate) appears to be best suited as a protective shell for highly selective palladium-colloid catalysts. The preferred support is $CaCO_3$. The Pd(SB12) colloids supported on $CaCO_3$ show the highest selectivities and activities of all tested catalysts. The best selectivity (98.1%) towards the desired cis-3-hexen-l-ol (leaf alcohol) is obtained with a lead acetate-promoted palladium-colloid supported on $CaCO_3$. This catalyst was shown to be slightly (0.5%) better in selectivity, but twice as active as a conventional Lindlar catalyst.

7.2 Oxidation

Bimetallic, even multimetallic precursors on various supports, whether or not promoted by dopants, have successfully been tested to be highly active, selective oxidation catalysts of remarkable durability. For example, surfactant-stabilized Pd-Pt-charcoal catalysts, promoted by bismuth were proved to be superior catalysts for the carbohydrate oxidation reaction shown in Fig. 13.
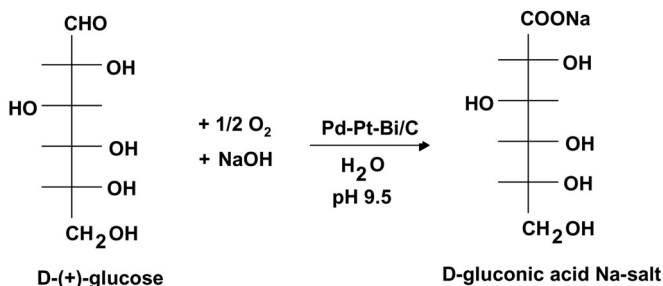
Fig. 13: Carbohydrate oxidation reaction

Charcoal-supported Pd_{88}/Pt_{12}-N(Octyl)$_4$Cl alloy particles show an excellent activity combined with high selectivity in the oxidation of glucose to gluconic acid when compared to industrial heterogeneous Pd/Pt catalysts. An increased durability of the colloidal catalysts was also observed. Much greater retention of the catalytic activity was found for such a system as compared to a conventionally manufactured Pd/C catalyst after recycling both catalysts 25 times under similar conditions. Obviously, the lipophilic (Octyl)$_4$NCl surfactant layer prevents the colloid particles from coagulating and being poisoned in the alkaline aqueous reaction medium. According to TEM, XRD/DFA, XPS, XANES, and EXAFS analysis the chemical coreduction of $PdCl_2$ and $PtCl_2$ in the appropriate ratio with N(Octyl)$_4$B(Ethyl)$_3$H yielded the alloyed Pd/Pt colloids in organic solvents. They are effectively screened by the lipophilic N(Octyl)$_4$Cl surfactant layer from coagulation and poisoning. TEM showed particle sizes in the range from l .5nm to 3nm.

7.3 Fuel Cell Catalysts [13]

Fuel cell technology attracts a great deal of interest because it allows the direct conversion of chemical energy into electricity. The catalyst systems are an integral part of the electrochemical reactor utilized in fuel cells. Among the wide-ranging applications of fuel cells are low-emission transport systems, stationary power stations, and combined heat and power sources. Classical studies were carried out in the early 1900s and major innovations and improvements have been achieved over the last few years. The first "new electric cars" are expected to be on the market around 2005, but further developments are still needed, most notably in the area of catalysts. Hydrogen fuel cell catalysts rely on pure Pt, whereas Pt alloy electrocatalysts are employed for the conversion of reformer gas or methanol into electricity. The active components in the latter cases are small, Pt-containing bi- or trimetallic particles, 1 – 3nm in size, which scatter X-rays as nearly perfect "single crystals". These systems offer improved efficiency and tolerance towards certain contaminants, especially CO, in the anode feed. It was clear from patents filed in the early 1970s that finely particulate colloidal platinum sols should be the ideal precursors for the manufacture of fuel cell electrodes.

This section focuses on recent developments in catalysts for proton-exchange membrane fuel cells (PEMFCs). PEM fuel cells use a solid proton-conducting polymer as the electrolyte at 50 – 125°C. The cathode catalyst is based on Pt alone, but because of the required tolerance to CO a combination of Pt and Ru is preferred for the anode. Colloidal Pt/Ru catalysts, as shown in Fig. 14, are currently under widespread investigation for low-temperature (80°C) polymer membrane fuel cells (PEMFCs). They have also been proposed for use in direct methanol fuel cells (DMFCs) or in PEMFCs, which are fed with CO-contaminated hydrogen produced in on-board methanol reformers. The ultimate dispersion state of the metals is essential for CO-tolerant PEMFCs, and truly alloyed Pt/Ru colloid particles, less than 2nm in size, seem to fulfill these requirements. Alternatively, bimetallic Pt/Ru PEM catalysts have been developed for the same purpose, where non-alloyed Pt nanoparticles of <2nm and Ru particles of <1nm are dispersed on a carbon support. From the results obtained, it can be concluded that a Pt/Ru interface is essential for the CO tolerance of the catalyst, irrespective of whether the precious metals are alloyed.

Particle sizes of 1 – 2nm are accessible via coreduction using either triethylhydroborate or trialkylaluminum as reducing agents. Synthesis of the metallic colloid precursors, followed by supporting of the precursors on a commercial carrier (*e.g.* Vulcan XC 72), and removal of the stabilizing shell of the colloidal particles through thermal conditioning, results in highly active fuel cell catalysts. The precursor concept provides (Fig. 11) an excellent tool for the preparation of polymetallic PEM and DMFC catalysts of a wide range of Pt/M bimetallic mixtures. In addition, "surface doping" with a third metal is also possible as indicated in Fig. 14 a+b.
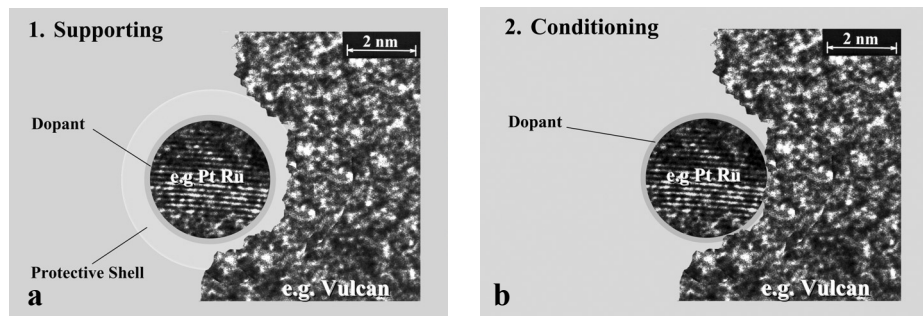
Fig. 14a+b: Preparation of plurimetallic fuel cell catalyst

Glassy carbon supported $Pt_{50}/Ru_{50}(Octyl)_4NCl$ colloids were examined by CO-stripping voltammetry and the data were found to be essentially identical to those found in well-characterized bulk-alloy electrodes. The activity of the colloid in the continuous oxidation of 2% CO in H_2 at a rotating disk electrode was determined at 25°C in 0.5 M H_2SO_4. The results led to the conclusion that these Pt/Ru colloids are very suitable precursors for high-surface-area fuel cell catalysts. XANES data were supportive of the bimetallic character of the particles. In addition, in situ XRD (by Debye function analysis) has revealed the catalytic function of the alloyed Ru in the CO oxidation: Oxide species are formed on the Ru surface at 280°C, which slowly coalesce to form RuO_2 particles. After re-reduction, the catalyst shows a pure *hcp* ruthenium phase and

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larger platinum-enriched alloy particles. Scanning probe microscopy (SPM) has been applied in order to characterize the real-space morphology of the electrode surfaces of supported nanostructured metal colloids on the nanometer scale. Colloidal Pt_{50}/Ru_{50} precursors (<2nm) raise the tolerance to CO, allowing higher CO concentrations in the H_2 feed of a PEMFC without a significant drop in performance. The colloid method was found to offer a highly suitable exploratory approach to finding improved formulations for binary and ternary anode electrocatalysts. The metals used include Pt, Ru, W, Mo, and Co. The combinatorial screening method has been successfully applied to electrocatalysts, [44, 45] and it is an obvious step to include colloids in these experiments.

Nanostructured metal colloids are very promising precursors for manufacturing multimetallic fuel cell catalysts that are truly nanosized (i.e. <3nm) and have high metal loadings (30 wt-% of metal).

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New Nanochemistry Items - *Metal Nanoclusters*

22-0095	Titanium cluster, tetrahydrofuran adduct (min. 40% Ti)	250mg
	>0.8 nm; dark brown solid *pyrophoric*	1g

Technical Note:
1.   Soluble in THF and ether. Insoluble in pentane and aromatics. Hydrogen storage catalyst.
References:
1.   *J. Am. Chem. Soc.*, **1996**, *118*, 12090.
2.   *Adv. Materials*, **2003**, *15*, 1012.

22-0090	Titanium cluster, tetrahydrofuran adduct (min. 25% Ti)	250mg
	>0.8 nm; dark brown solid *pyrophoric*	1g

Technical Note:
1.   Soluble in THF and ether. Insoluble in pentane and aromatics. Hydrogen storage catalyst.
References:
1.   *J. Am. Chem. Soc.*, **1996**, *118*, 12090.
2.   *Adv. Materials*, **2003**, *15*, 1012.

79-2010	Hexachlorodecakis(triphenylphosphine)pentapentacon-gold, 99%	100mg
		500mg
	$Au_{55}[P(C_6H_5)_3]_{12}Cl_6$; ca. 2 nm; FW: 14,193.30; dark brown solid	

Technical Note:
1.   Soluble in dichloromethane and pyridine. Insoluble in hydrocarbons, benzene and alcohols.
Reference:
1.   *Inorg. Synth.*, **1990**, *7*, 214.

New Nanochemistry Items – *Metal Nanocolloids*

78-0055	Platinum/tetra-n-octylammonium chloride colloid, purified (70-75% Pt)	250mg
		1g
	2.8 nm ±0.5nm; grayish-black pwdr. *pyrophoric*	

Technical Note:
1.   Soluble in THF. Insoluble in toluene, acetone, ether and ethanol.
References:
1.   *J. Mol. Catal.*, **1994**, *86*, 129.
2.   *Eur. J. Inorg. Chem.*, **2001**, 2455.
3.   *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 10, Chapter 20, p. 209-223, Theime Verlag, NY, **2002**.
4.   *Catalysis and Electrocatalysis at Nanoparticles Surfaces*, Chapter 10, p. 343-377, Marcel Dekker, NY, **2003**.

45-1660	Rhodium/tetra-n-octylammonium chloride colloid, purified (70-75% Rh)	250mg
		1g
	2.0 nm ±0.5 nm; gray pwdr. *pyrophoric*	

Technical Note:
1.   Very soluble in THF, soluble in acetone, slightly soluble in toluene, insoluble in ether.
References:
1.   *J. Mol. Catal.*, **1994**, *86*, 129.
2.   *Eur. J. Inorg. Chem.*, **2001**, 2455.
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4.   *Advanced Catalysts and Nanostructured Materials*, Chapter 7, Academic Press, San Diego, **1996**, 165-196.

28-0008	Nickel/tetra-n-octylammonium chloride colloid, purified (65-70% Ni)	250mg
		1g
	2.8 nm (average); black pwdr. *pyrophoric*	

New Nanochemistry Items – *Metal Nanocolloids (cont.)*

Technical Note:
1.   Soluble in THF, toluene, acetone and methylene chloride. Insoluble in ethanol, ether and pentane.

References:
1.   *J. Mol. Catal.*, **1994**, *86*, 129.
2.   *Eur. J. Inorg. Chem.*, **2001**, 2455.
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4.   *Advanced Catalysts and Nanostructured Materials*, Chapter 7, Academic Press, San Diego, **1996**, 165-196.

79-0080	Gold/tetra-n-octylammonium chloride colloid	250mg
	2.6 nm ±1.1 nm; brown-orange solid	1g

Technical Note:
1.   Soluble in toluene. Precursor for CO-oxidation catalysts.

78-0062	Platinum-ruthenium/tetra-n-octylammonium chloride colloid (~7 wt% Pt, ~3.5% wt% Ru)	250mg
		1g
	1.7 nm ±0.5nm; waxy, black residue	

Technical Note:
1.   Very soluble in THF. Soluble in toluene. Precursor for fuel cell catalysts.

References:
1.   *J. Mol. Catal.*, **1994**, *86*, 129.
2.   *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 10, Chapter 20, p. 209-223, Theime Verlag, NY, **2002**.
3.   *Catalysis and Electrocatalysis at Nanoparticles Surfaces*, Chapter 10, p. 343-377, Marcel Dekker, NY, **2003**.

78-0011	Platinum colloid (polyethyleneglycol-dodecylether hydrosol) (~10 wt% Pt)	1g
		5g
	1.2 nm ±0.3; brown-black viscous substance	

Technical Note:
1.   Soluble in ether, alcohol, water and aqueous solutions.

Reference:
1.   *Eur. J. Inorg. Chem.*, **2001**, 2455.

45-1550	Rhodium colloid (polyethyleneglycol-dodecylether hydrosol) (~9 wt% Rh)	1g
		5g
	~2 nm; brown-black viscous substance	

Technical Note:
1.   Soluble in ether, alcohol, and water.

Reference:
1.   *Eur. J. Inorg. Chem.*, **2001**, 2455.

78-0060	Platinum-ruthenium colloid (polyethyleneglycol-dodecylether hydrosol)	1g
		5g
	1.3 nm (average); brown-black substance	

Technical Note:
1.   Soluble in toluene, ether, THF, ethanol, acetone and water.

References:
1.   *Eur. J. Inorg. Chem.*, **2001**, 2455.
2.   *Catalysis and Electrocatalysis at Nanoparticles Surfaces*, Chapter 10, p. 343-377, Marcel Dekker, NY **2003**.

New Nanochemistry Items - *Metal Nanoparticles*

27-0020	Cobalt nanoparticles	1g
	10-12 nm; black pwder	5g

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New Nanochemistry Items - *Metal Nanoparticles (cont.)*

Technical Note:
1.   Used for powder metallurgy.
References:
1.   *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2.   H. Bönnemann, et. al., DE 10227779.6
3.   *Magnetohydrodynamics*, **2003**, *39*, 29.

| 27-0026 | Cobalt nanoparticles, toluene wet | 1g |
| | 10-12 nm; black suspension | 5g |

Technical Note:
1.   Suspension in toluene. Precursor for magnetic fluids.
References:
1.   *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2.   H. Bönnemann, et. al., DE 10227779.6
3.   *Magnetohydrodynamics*, **2003**, *39*, 29.

27-0023	Cobalt nanoparticles coated with AOT [sodium dioctyl-	1g
	sulfosuccinate]	5g
	10-12 nm; black waxy material	

Technical Note:
1.   Dispersed in toluene, kerosene, mineral oil. Precursor for magnetic fluids.
References:
1.   *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2.   H. Bönnemann, et. al., DE 10227779.6
3.   *Magnetohydrodynamics*, **2003**, *39*, 29.

| 26-0011 | Iron-cobalt nanoparticles | 250mg |
| | 5-8 nm; black pwdr. | 1g |

Technical Note:
1.   For powder metallurgy purposes.

New Nanochemistry Items - *Metal Nanopowders*

| 78-0007 | Platinum, 97% (2-5 nanometers) | 250mg |
| | black pwdr. *pyrophoric* | 1g |

Reference:
1.   *J. Mol. Catal.*, **1994**, *86*, 129.

| 78-0009 | Platinum, min. 90% (5-13 nanometers) | 250mg |
| | black pwdr. | 1g |

References:
1.   French Patent #8221483, 1985.
2.   *Solid State Ionics*, **1989**, *32/33*, 198.
3.   *Fine Particles, Synthesis, Characterization and Mechanisms of Growth*, Marcel Dekker, NY, **2000**, 460-496.

New Nanochemistry Items - *Magnetic Fluids*

1.   We use toluene and light mineral oils as the solvent base.
2.   Our products are stable dispersions of mono-dispersed metallic cobalt and iron particles.
3.   Our products have particle concentrations of less than 9 vol%, magnetizations up to 150 millitesla, and low viscosities.

27-0017	Cobalt magnetic fluid in toluene stabilized with LP4	1ml
	[a fatty acid condensation polymer] (ca. 4 vol%)	5ml
	ca. 10 nm (mean particle size); black fluid	25ml

Technical Note:
1.   Carrier liquid is toluene. Miscible with mineral oils. Magnetization – 59 kA/m (74 mT).
References:
1.   *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2.   H. Bönnemann, et. al., DE 10227779.6
3.   *Magnetohydrodynamics*, **2003**, *39*, 29.

New Nanochemistry Items - *Magnetic Fluids (cont.)*

27-0014	Cobalt magnetic fluid in toluene stabilized with cashew oil	1ml
		5ml
	ca. 10 nm (mean particle size); black fluid	25ml

Technical Note:
1. Carrier liquid is toluene. Miscible with mineral oils.
References:
1. *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2. H. Bönnemann, et. al., DE 10227779.6
3. *Magnetohydrodynamics*, **2003**, *39*, 29.

27-0001	Cobalt magnetic fluid in kerosene with AOT [sodium dioctylsulfosuccinate] and LP4 [a fatty acid condensation polymer] (8.2 vol%)	1ml
		5ml
		25ml
	ca. 10 nm (mean particle size); black fluid	

Technical Note:
1. Carrier liquid is kerosene. Miscible with mineral oils. Magnetization – 119 kA/m (150 mT).
References:
1. *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2. H. Bönnemann, et. al., DE 10227779.6
3. *Magnetohydrodynamics*, **2003**, *39*, 29.

27-0011	Cobalt magnetic fluid in kerosene with LP4 [a fatty acid condensation polymer] (ca. 4 vol%)	1ml
		5ml
	ca. 10 nm (mean particle size); black fluid	25ml

Technical Note:
1. Carrier liquid is kerosene. Miscible with mineral oils. Magnetization – 57.4 kA/m (72 mT).
References:
1. *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2. H. Bönnemann, et. al., DE 10227779.6
3. *Magnetohydrodynamics*, **2003**, *39*, 29.

27-0007	Cobalt magnetic fluid in kerosene with cashew oil and LP4 [a fatty acid condensation polymer] (3.2 vol%)	1ml
		5ml
	ca. 10 nm (mean particle size); black fluid	25ml

Technical Note:
1. Carrier liquid is kerosene. Miscible with mineral oils. Magnetization – 47 kA/m (59 mT).
References:
1. *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2. H. Bönnemann, et. al., DE 10227779.6
3. *Magnetohydrodynamics*, **2003**, *39*, 29.

27-0004	Cobalt magnetic fluid in kerosene with cashew oil	1ml
	ca. 10 nm (mean particle size); black fluid	5ml
		25ml

Technical Note:
1. Carrier liquid is kerosene. Miscible with mineral oils.
References:
1. *Inorganica Chimica Acta.*, **2003**, *350*, 617.
2. H. Bönnemann, et. al., DE 10227779.6
3. *Magnetohydrodynamics*, **2003**, *39*, 29.

26-0017	Iron-cobalt magnetic fluid in toluene stabilized with cashew oil (0.19 vol%)	1ml
		5ml
	ca. 7 nm (mean particle size); black fluid	25ml

Technical Note:
1. Carrier liquid is toluene. Magnetization – 4.7 kA/m (5.9mT).

26-0015	Iron-cobalt magnetic fluid in kerosene stabilized with cashew oil and LP4 [a fatty acid condensation polymer]	1ml
		5ml
	ca. 7 nm (mean particle size); black fluid	25ml

Technical Note:
1. Carrier liquid is kerosene.

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