Innovation in fine chemical synthesis by novel polymer-based catalysts in conjunction with microflow reactor architectures

Catalysis is pivotal to our society. The availability of both inexpensive bulk materials and specialized fine chemicals is based on industrial catalytic processes. Additionally the development of highly specialized catalysts is the key to new technologies for sustainable production and environmental protection. These determining factors are the reason for our EU funded project POLYCAT. It stands for the innovative use of novel polymer-based nanoparticulate catalysts combined with the outstanding properties of mirostructured reactor architectures, both novel and sustainable technologies in the field of catalysis.

Our consortium of 19 academic and industrial partners allies the profound expertise in the fields of target-directed synthesis, high detailed analysis, and theoretical in-silico calculations of catalytical processes. Besides the chemically oriented aspects of the project also economic and environmental impacts of our newly developed materials and processes are surveyed with Cost Analyses and Life Cycle Assessments. Our industrial partners contribute to the success of the POLYCAT project by the development of advanced microstructured reactors and the demonstration of our novel synthesis tools implemented into their process chains. The overall project issues can be outlined by the following directives:

- Using highly selective catalysts and alternative solvents
- Developing new synthetic reactions with novel process parameters
- Improving the resource efficiency by higher selectivity for reduced waste and emissions
- Applying environmentally benign processes for higher eco-efficiency

The POLYCAT project started in October 2010 and is coordinated by the Institut für Mikrotechnik Mainz GmbH (IMM). The 3.5 years project is partly funded by the European Commission with a grant of 7 million € in the context of the EU Seventh Framework Programme for Research and Technology Development (Contract CP-IP 246095-2).

In the course of this first POLYCAT newsletter we like to focus on the basic ideas for the application of polymer-based and nanoparticulate catalysts by means of their advantages and striking characteristics. The following five articles give an overview on the polymeric materials used and developed at our partners’ laboratories for the synthesis of such novel catalysts. Beside advancements in the use of well-known carbon nanotubes and hypercrosslinked polystyrene derivatives, also stimuli-responsive microgels and polyelectrolyte-based materials are discussed as well as dendron- and dendrimer-functionalized iron oxide particles. Although not covered in this newsletter the POLYCAT consortium also develops reactor and plant concepts for the future application of such novel catalyst materials.

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Dr. Patrick Lüb, Coordinator of POLYCAT
Heading the Mixing and Fine Chemistry Department at IMM he is much experienced with EU projects. His main focuses are the development and realisation of milli- and micro-reactors, their implementation for chemical processes and the setup of corresponding plants.

Dr. Thomas Rehm, Technical Project Manager of POLYCAT
Coming originally from bioorganic and supra-molecular polymer chemistry he joined POLYCAT as Technical Project Manager and Work Package Leader. Beside the administrative jobs he works on novel coating procedures for microstructured reactors used in catalysis.
Carbon is a widely used support material for heterogeneous catalysts as it possesses several advantages including a low price, high surface area and chemical inertness towards a broad range of reaction or process conditions. When precious metals are supported on carbon the easy recovery of these valuable components by simply burning off the carbon support represents a further important advantage of carbon based support materials. On the other side this sensitivity of carbon in oxidative environments limits its applicability to reactions and processes, where combustive degradation will not occur.

Since their discovery 1991 carbon nanotubes (CNT) – one of the five carbon allotropes known today – have received a continuously growing interest by the scientific community. Similar to graphite, carbon nanotubes have a honeycomb structure made up of hexagonal carbon rings. These honeycomb shapes form tubes with defined diameters consisting of one (single-walled CNT) or several walls (multi-walled CNT). The unique physical and chemical properties of CNT make them suitable for a tremendous variety of applications. Accordingly, the market potential of CNT is estimated at several thousand tons annually for the next few years. This has driven intense efforts towards the development of industrial processes that allow for large scale production of high quality carbon nanotubes. For example, Bayer has launched a research plant allowing for CNT production at a 200 t/year scale in 2010. In Bayer process CNT are produced in high quality by catalytic chemical vapor deposition (CCVD) of carbon containing precursors in a fluidized bed reactor. Figure 1 (left) shows a transmission electron microscopy (TEM) image of a typical CNT sample.

The properties of carbon nanotubes can be tuned and adapted to specific needs by the introduction of heteroatoms. Accordingly, Nitrogen-doped carbon nanotubes (NCNT) are formed when nitrogen containing precursor molecules are used in the CCVD process (Figure 1, right).

Several specific advantages of CNT or NCNT as compared to conventional activated carbon materials render them highly attractive for their application as support material for metallic catalyst phases. The comparatively high stability under oxidizing conditions extends the process window where (N)CNT-supported catalysts can be used. Strong electronic interactions between the (N)CNT support and the metal improves adhesion of the catalytically active metal phase to the carbon surface thereby promoting the catalytic activity of the metal nanoparticles as well as reducing the amount of metal leaching or sintering. The high surface area (approx. 200 to 300 m²/g) in combination with the open and mesoporous structure of this material class are further benefits for application in heterogeneous catalysis as they ensure both excellent transport properties and easy access of the reactants to the catalyst particles thereby accelerating the respective reactions. This may allow for lower metal amounts needed to obtain the desired activities. The presence of nitrogen atoms within nitrogen-doped carbon nanotubes supports provides an additional chemical functionality, i.e. basicity, that further increases metal-support interactions in the resulting catalysts and may also result in cooperative catalytic effects in the respective reaction. The exact chemical nature of the nitrogen functionality within the carbon structure (neutral, cationic, ring size of nitrogen containing ring) can be tailored by appropriate selection of the synthesis conditions applied for NCNT preparation. Accordingly, the degree to which the properties of the NCNT material can be adapted to specific needs is further extended, when NCNT are used as catalyst support.
Figure 2 shows transmission electron microscope images of catalysts, which were prepared by supporting Ru nanoparticles onto both CNT and NCNT support materials. Depending on the method of preparation the size of the resulting metal nanoparticles can be controlled (e.g. 1.3 (± 0.2) nm, Ru/CNT (left) or 2.7 (± 0.3) nm, Ru/NCNT (right). Ru/(N)CNT catalysts are especially suitable for application in hydrogenation reactions, which represent one of the major industrial processes. Within POLYCAT Bayer Technology Services GmbH is currently investigating the activity of Ru/CNT and Ru/NCNT catalysts in the hydrogenation of glucose to sorbitol.

The consortium member Helmholtz-Zentrum Berlin (HZB) is active in the preparation and characterization of catalysts with a core shell structure of the carrier material onto which different metal nanoparticles are immobilized. As the core material, HZB uses (crosslinked) polystyrene or inorganic silica. To access excellent stability in environmentally benign solvent / water mixtures, the shell is made of a positively or a negatively charged polyelectrolyte. Depending on the experimental approach, the water soluble polymer can be attached by a grafting approach (polyelectrolyte brush, see Figure 1) or by crosslinking (microgel, not shown). Those systems have been studied in detail for more than ten years.[1] Depending on the nature of the polyelectrolyte, different metal nanoparticles can be immobilized ranging from Ni and Ru on anionic poly (acrylic acid) brushes to Pd, Au and Pt on cationic polyelectrolyte brushes (Figure 1). In the TEM micrograph, the well dispersed Pd-nanoparticles can be seen as darker spots on the spherical polystyrene particles. The benefit of the carrier architecture is attributed to the following advantages:

- there is almost no mass transfer limitation through an extended ultrathin (100 nm) polymeric shell since the diffusion time within the polymer network is in the range of milliseconds, [2]
- leaching of the metal into solution may be reduced by means of an interaction between polymer chains and metal nanoparticles [3] and
- the catalyst can be easily recovered by ultrafiltration after use. [4]

In principle, this makes the HZB catalysts promising candidates for a variety of industrially relevant reactions like the Suzuki coupling [4] or the selective hydrogenation of sugar compounds. The application of our catalysts within POLYCAT requires an irreversible attachment to microchannel walls like stainless steel surfaces modified with Al2O3 or SiO2. As a strategy the use of electrostatic interactions, polycondensation or additional functional monomers is followed.


Metal nanoparticles within functional ultrathin polymer layers

The consortium member Helmholtz-Zentrum Berlin (HZB) is active in the preparation and characterization of catalysts with a core shell structure of the carrier material onto which different metal nanoparticles are immobilized. As the core material, HZB uses (crosslinked) polystyrene or inorganic silica. To access excellent stability in environmentally benign solvent / water mixtures, the shell is made of a positively or a negatively charged polyelectrolyte. Depending on the experimental approach, the water soluble polymer can be attached by a grafting approach (polyelectrolyte brush, see Figure 1) or by crosslinking (microgel, not shown). Those systems have been studied in detail for more than ten years.[1] Depending on the nature of the polyelectrolyte, different metal nanoparticles can be immobilized ranging from Ni and Ru on anionic poly (acrylic acid) brushes to Pd, Au and Pt on cationic polyelectrolyte brushes (Figure 1). In the TEM micrograph, the well dispersed Pd-nanoparticles can be seen as darker spots on the spherical polystyrene particles. The benefit of the carrier architecture is attributed to the following advantages:

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Functional microgels as nanoreactors for the development of novel heterogeneous nanoparticulate catalysts

The involvement of Foundation of Research and Technology – Hellas (FORTH) in the POLYCAT project focuses on the development of novel microgel-based nanoparticulate catalysts for immobilization onto the microreactor walls. Microgels are intramolecularly cross-linked macromolecules with a globular shape and with a diameter of a few hundred nanometers that form a stable dispersion in numerous solvents (see Figure 1). In our approach, functional polymer microgel particles have been employed as templates for the growth of catalytically active metal nanoparticles (NPs). The use of microgel supported metal nanocatalysts possesses certain advantages over other polymer supported catalytic systems, which are related to their facile synthetic procedure via aqueous emulsion copolymerization of a monomer with a cross-linker in the presence of a stabilizer, their enhanced colloid stability over a wide pH range, their use in a wide range of organic and aqueous solvents and their ability to exhibit a stimulus-responsive behavior to a variety of external stimuli.

The role of the microgel material is mainly in enhancing the stability, reactivity and selectivity of the metal nanocatalysts in comparison to their bulk counterparts. This reduces production costs, increases the quality of the target product and provides environmentally friendly catalytic systems that can operate both in organic and aqueous media. Moreover, functional microgel-stabilized nanocatalysts allow the facile separation and reuse of the catalyst.

The synthetic approach of FORTH involves first the synthesis of microgels tailored with appropriate functional pendant groups that will act as anchoring points for the immobilization of the heterogeneous nano-catalysts. Next, metallic NPs are formed within the polymeric microgels by the interaction of the metal precursor functional groups with metal precursor compounds, followed by metal reduction to produce the metal impregnated NPs (see Figure 1). Monometallic as well as bimetallic NPs can be prepared by this method using one or a combination of appropriate metal precursor molecules.

FORTH has prepared two type of pH responsive microgel particles based on polyacidic (poly(methacrylic acid), PMAA, and poly(acrylic acid), PAA) and polybasic (poly(2-(diethylamino)ethyl methacrylate), PDEAEMA) functionalities comprising carboxylic acid and tertiary amine-based functionalities, respectively (see Figure 2).

The size of the microgel particles prepared are in the range of 100-260 nm (see Figure 3) and can be varied on demand by changing the mono-mer/stabilizer molar feed ratio upon microgel synthesis.

These microgel particles have been used as ‘nano-reactors’ for the formation of gold (Au), palladium (Pd)
and ruthenium (Ru) NPs. Au and Pd NPs with an average diameter of 3 nm have been homogenously formed within the PDEAMA microgel particles (see Figure 4) whereas Ru NPs were incorporated within the acidic (PAA and PMAA) microgels.

These metal nanoparticle containing microgels can be immobilized onto the microreactor walls for nanocatalyst use under flow conditions (see Figure 5). The attachment is based on the interaction of the functional moieties of the microgels with the microchannel surface via van der Walls, complexation or electrostatic interactions.

FORTH has investigated the immobilization of the metal nanoparticle containing microgel particles on model surfaces, i.e., silicon and glass. SEM images show the formation of mono and multi-layers of the PMAA microgel particles on the glass substrates (see Figure 6). The durability, stability and viability of the microgel particles on the surfaces is also studied under flow conditions.

### Novel polymer-based nanocatalysts applying hypercrosslinked polystyrene

Nowadays, industrial chemical syntheses of vitamins and pharmaceuticals include at least one catalytic stage. The most important problem in industrial catalysis is the achieving of high selectivity, activity and technological performance of catalytic systems. This strongly stimulates the search for new catalytic systems, which might combine the advantages of both heterogeneous and homogeneous catalysts.

The TTU group developed novel polymer nanocatalysts based on hypercrosslinked polystyrene (HPS). HPS is a highly porous polymer with rigid cavities, the size of which can be varied depending on the reaction conditions. HPS is produced by Purolite Ltd (U.K.) as a sorbent but HPS can be also used for controlled formation of catalytic nanoparticles (NPs).

HPS based catalysts allow control over NP formation due to a “cage” effect (by limiting the NP size via the pore size) along with controlling the precursors and reduction conditions. It is noteworthy that HPS matrix also provides excellent stability of the catalysts developed due to trapping NPs and preventing leaching of metal species. The above advantages of HPS-based catalysts allow regeneration and multiple reuse of the catalysts developed and thus seem to be especially promising for exploitation in industry.
In the framework of POLYCAT project TTU developed mono- (Pt, Pd, Ru, Au) and polymetallic (Pd-Pt, Pd-Zn, Pd-Au-Zn, etc.) HPS-based catalytic systems using various commercial HPS (non-functional, HPS materials bearing amino- and sulfo-groups). Besides, the nature of the metal precursor compounds was varied [1] to design nanoparticulate catalysts containing monodisperse NPs.

The catalytic systems developed were tested in reactions of fine organic chemistry of both fundamental and industrial importance: oxidation of mono- [2] and disaccharides, hydrogenation of monosaccharides, Lindlar-type hydrogenation of acetylene alcohols. For all the reactions studied, promising results were obtained with HPS-based catalysts.

To illustrate the behavior of the catalysts developed, a few examples are provided. For one, in the case of selective hydrogenation of a C5 acetylene alcohol (an intermediate product in the synthesis of vitamins A, E, K and fragrant substances), 0.1 %-Pd/HPS catalyst (Fig. 2) provides selectivity higher than 97 % (at 100 % conversion) which significantly exceeds the selectivity of conventional industrial catalysts (e.g. Lindlar catalyst) at higher metal loading, with the use of hazardous modifiers and metal leaching.

The other reaction of interest where the HPS-catalysts were tested is the syntheses of ultrapure D-gluconic acid by oxidation of D-glucose over gold NPs incorporated in HPS (1 %-Au/HPS).

The use of Au/HPS catalyst characterized by high stability in multiple reaction cycles resulted in the 98-99 % yield of gluconic acid.

Ru-containing HPS is a prospective catalyst of D-glucose selective hydrogenation for sorbitol production. The high resolution transmission electron microscopy (HRTEM) image of a single Ru particle is presented in Figure 3. The use of 3 %-Ru/HPS leads to a selectivity >98 % at 100 % of glucose conversion without use of any modifiers, formation of side-products, pollution of the target product with N2O ions as occurs with the conventional saccharide hydrogenation catalyst-, or Ni-Raney.

The general advantages of HPS-based catalytic systems developed by TTU in POLYCAT project in comparison with existing industrial catalysts include:

- large specific surface area (usually near 1000-1500 m²/g);
- possibility to work in virtually any solvent;
- high catalyst activity at lower metal loading due to formation of well-defined NPs vs. their aggregation in conventional catalysts;
- higher stability and lifetime due to the minimization of metal loss;
- high selectivity without necessity to use catalytic poisons and metal-modifiers;
- prevention of NP aggregation during the reaction.


The group at the A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS) developed a family of novel polyphenylene-epyrild dendrimers and dendrons using Diels-Alder condensation of ethynyl derivatives and substituted cyclopentadienones. The structure of dendrimers and dendrons was varied to determine the influence of the dendron/dendrimer periphery and the dendron focal groups on the formation of magnetic nanoparticles to be used in the development of magnetically recoverable catalysts. Figure 1 shows examples of dendrons and dendrimers with pyridyl periphery.

The example of the dendron decorated with long hydrophobic tails on the periphery is presented in Figure 2. Such a dendron will allow additional stabilization of nanoparticles coated with dendrons due to the absence of exchange between the dendron shells. It is expected that it will also lead to the formation of ultra small catalytic nanoparticles after incorporation of catalytic species in the shells of magnetic nanoparticles.

The high thermal stability of the dendrimers and dendrons allows their use in the formation of iron oxide nanoparticles via high-temperature organometallic routes leading to higher quality magnetic nanoparticles. In particular, the dendrons and dendrimers shown in Figure 1 were used in the syntheses of Fe3O4 nanoparticles from iron acetylacetonate. Figure 3 shows transmission electron microscopy (TEM) images of the Fe3O4 nanoparticles stabilized by the dendrons shown in Figure 1a and the dendrimers shown in Figure 1b. One can see that nanoparticles prepared in the presence of the third generation dendrimers containing pyridyl groups both in the interior and periphery allows formation of flower-like arrangement of nanoparticles due to multiple coordinating sites of the single dendrimer molecule.

The interaction of Fe3O4 nanoparticles stabilized by the above dendrimers leads to the formation of particle aggregates (Figure 3c) after interaction with Pd acetate. Apparently Pd complexes are formed between the dendrimers located on the neighboring Fe3O4 nanoparticles. This aggregation is beneficial because it allows fast magnetic separation of the catalysts from the reaction solution in catalytic reaction. These catalysts were tested in selective hydrogenation of dimethyl-ethynylcarbinol to dimethylvinylcarbinol and showed promising results with selectivity reaching 97%.

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Interdisciplinary team from industry and academia allies the expertise in the fields of polymer chemistry, nanoparticle-based catalysis and microreactor engineering.

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