Synthesis and catalytic activity of metal nanoclusters inside functional resins: an endeavour lasting 15 years

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Cross-linked functional polymers (functional resins) are versatile, designable and useful supports for metal nanoclusters that are able to provide reasonably thermally and mechanically stable multi-functional metal catalysts characterized by good activity and selectivity. The paper reviews authors’ contributions to the field from the early 1990s to the present.

Keywords: nanotechnology; metal clusters; catalysis

1. Introduction

Nanostructured metal particles (commonly called metal nanoclusters; Zecca et al. 2008), typically dispersed on inorganic metal oxides or active carbon microparticles, provide mankind with the largest class of technologically useful catalysts (Ertl et al. 1997). The role of the support is primarily physical in nature, but chemical interactions with the metal nanoclusters (Schmid & Corain 2003) or co-catalytic effects exerted by the support itself (Volkmar et al. 2009) are well documented in the literature.

Prospects of the development of a catalytic chemistry based on an active and designed role of the support are shown in scheme 1.

We can imagine the synthesis and the use of sophisticated $M^0$/CFP (cross-linked functional polymers) catalysts able to operate with diverse metal centres and diverse functional groups for promoting multi-step sequential syntheses (scheme 1) otherwise unattainable with conventional catalysts.

In fact, bi- or, possibly, multi-functionality is a useful potentiality for metal catalysts made just of a nanoclustered metal component, hereafter referred to as $M^0$, and of a functional support, hereafter referred to as $S(F)$. The ‘functionality’ of $M^0$ and the ‘functionality’ featuring $S(F)$ may exert a quite useful dual

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function, in a cascade fashion, as, for example, in the case of Pd⁰/S(F) catalysts, in which S(F) is a Brönsted or Lewis acidic inorganic material (Barrett et al. 2006; Brito et al. 2007; Nie et al. 2007; Trasarti et al. 2007; Guo et al. 2008; Hetterley et al. 2008; Rezai & Traa 2008; Seki et al. 2008).

A remarkably simple (and fortunate) example of these catalysts was discovered in the 1960s by two German technologists, i.e. Wöllner and Neier (Wöllner & Neier 1966), who patented, for Bergbau Chemie, the use of cross-linked strongly acidic polymers (ion-exchange resins) as acidic supports for Pd⁰ nanoclusters. The obtained materials turned out to be suitable bi-functional catalysts for the chemoselective synthesis of the important industrial solvent methyl isobutyl ketone (MIBK) from acetone and dihydrogen (RWE-DEA process, 10 000 tonnes yr⁻¹, Cologne, Germany). The key feature in the catalysts was the simultaneous presence of two co-operative catalytic functionalities, i.e. the sulphonic groups and nanostructured Pd⁰, able to catalyse, in a cascade fashion, the condensation of acetone to mesitylene oxide (acid catalysis) and the hydrogenation of the latter (metal catalysis).

The vital message contained in this observation was appreciated by only a few scientists, including Gates (Hanson et al. 1974; Tibbitt et al. 1975), Frechet (Li & Fréchet 1985) and Toshima (Ohtaki et al. 1991), and it remained buried in the large catalysis-related literature until the early 1990s.

Gates and associates (Tibbitt et al. 1975) described an original chemoselective synthesis of acetone from propylene and water catalysed by Pt⁰ supported on a macroreticular sulphonic resin. Li & Fréchet (1985) described a very effective and chemoselective Pd⁰ catalyst supported on polybenzimidazole for the reduction of aliphatic and aromatic nitrocompounds to amines. Finally, Toshima and associates described a wide variety of hydrogenation reactions of functional olefins catalysed by Pt⁰ and Rh supported on a polyacrylamide gel (Ohtaki et al. 1991).

On the basis of this stimulating, albeit limited, literature, an extensive forward-looking project was proposed and pursued in the early 1990s in these laboratories, aimed at the following:

— developing the application of existing ‘analytical’ technologies to investigate the nanometre-scale structure of macroreticular and gel-type (GT) CFPs: inverse steric exclusion chromatography, ISEC (Jefábek 1985a,b), electron spin resonance (ESR) spectroscopy (Biffis et al. 1995), pulse field gradient spin echo NMR (PGSE-NMR) spectroscopy (D’Archivio et al. 1998) and cross-polarization magic angle spinning \(^{13}\)C-NMR (CP-MAS \(^{13}\)C-NMR) spectroscopy (Pozzar et al. 2005);

— developing simple synthesis protocols to M⁰/CFP;

— controlling the distribution of metal nanoclusters inside the body of resin particles;
Table 1. Selection of research groups active in the synthesis and exploitation of \( \text{M}^0/\text{CFP} \) catalysts (since 2000).

<table>
<thead>
<tr>
<th>promoted syntheses</th>
<th>reference</th>
</tr>
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<tbody>
<tr>
<td>L-sorbose oxidation</td>
<td>Sidorov et al. (2001)</td>
</tr>
<tr>
<td>oxidative carbonylation of amine to carbamates and symmetric ureas</td>
<td>Shi &amp; Deng (2002)</td>
</tr>
<tr>
<td>aerobic alcohols oxidation to aldehydes</td>
<td>Uozumi &amp; Nakao (2003)</td>
</tr>
<tr>
<td>synthesis of analgesic ((-\text{(2R,3R)}-[3-(3-methoxy-phenyl)-2-methylpentyl]-dimethyl-amine hydrochloride</td>
<td>Wissler et al. (2007)</td>
</tr>
<tr>
<td>hydroxylation of benzene with ( \text{O}_2 ) to phenol in the presence of ( \text{H}_2 )</td>
<td>Laufer &amp; Hoelderich (2002)</td>
</tr>
<tr>
<td>alcohols oxidation to aldehydes</td>
<td>Miyamura et al. (2007)</td>
</tr>
<tr>
<td>miscellaneous reactions</td>
<td>Ishida &amp; Haruta (2007)</td>
</tr>
<tr>
<td>chemoselective hydrogenation of ( \text{C}=\text{C} ) in crotonaldehyde to 2-ethylhexanal</td>
<td>Seki et al. (2008)</td>
</tr>
<tr>
<td>selective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone</td>
<td>Biffis et al. (2002)</td>
</tr>
<tr>
<td>direct synthesis of ( \text{H}_2\text{O}_2 ) in the absence of selectivity enhancers</td>
<td>Burato et al. (2009)</td>
</tr>
</tbody>
</table>

— exploring the catalytic potency of \( \text{Pd}^0/\text{CFP} \) in a variety of ‘simple’ hydrogenation reactions such as cyclohexene hydrogenation (Zecca et al. 2000; Centomo et al. 2009), chemoselective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone (Biffis et al. 2002) and direct synthesis of hydrogen peroxide (Burato et al. 2009);
— evaluating the possibility of a template effect of the swollen polymer framework on the size of the metal nanoclusters generated in its interior (Corain et al. 2004a).

Since 2000, the scientific community has started to investigate a number of very promising, sometimes irreplaceable (Wissler et al. 2007), innovative catalysts of \( \text{M}^0/\text{CFP} \) type (table 1).

In this article, we will review the main features of our contribution to the field and specifically outline some remarkable features generally relevant to its catalytic chemistry.

2. **Functional resins (cross-linked functional polymers)**

CFPs are isotropic organic materials, hereafter graphically referred to as \( \text{F}^-\text{F} \), resulting from the homo- or co-polymerization of (typically) vinyl monomers and from the cross-linking action of suitable divinyl co-monomers (scheme 2).
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Scheme 2. Example of vinyl monomer polymerization: co-polymerization of styrene and divinylbenzene to a polystyrene resin.

(a) Chemistry

The functional group $F$ may be chosen from among a variety of candidates and this choice is, of course, a key factor in imparting well-defined and potent chemical functions, the most known of which is certainly ion-exchange ability (Dorfner 1991). Among the functions of $F$, also very important is the metal co-ordination ability towards a variety of metal centres, $M^n$. The materials so obtained, $\Phi\text{-}F\text{-}M^n$, may be of interest for various applications. In particular, these materials might be quite useful ‘hybrid phase catalysts’ (Corain et al. 2004a). Another important and yet scarcely used opportunity offered by them is their reduction to catalytically active nanocomposites, $M^n\text{/}\Phi\text{-}F$ (Zecca et al. 2008; see §3a).

(b) Structure

By far the most representative and technologically relevant CFPs are categorized as GT and macroreticular (MA) materials. Both types of CFPs are commercially available as spherical beads (approx. 0.1–1.0 mm in diameter), whose shape is the result of a suspension polymerization procedure (Guyot 1988).

Both GT and MA materials are typically used in the so-called swollen state, i.e. a condition under which the dry polymer framework, owing to the absorption of suitable amounts of a given liquid medium driven by the solvation of the polymer chains, is converted into a sort of pseudo-solution of interconnected polymer chains (figures 1 and 2).

Remarkably, the absorption of the liquid phase generates an osmotic pressure that turns out to be balanced by the elastic counter-forces that are due to the existence of the cross-linking effect. The pseudo-solution state of a swollen resin particle is highlighted by the relatively high rotational mobility of probe molecules dissolved in the swelling medium (Biffis et al. 1995; D’Archivio et al. 1998) and by the significant translational mobility possessed by the solvent molecules confined inside the swollen polymer framework as well as by suitable translational probes (Corain et al. 2007).
Figure 1. (a) Metal catalysis on inorganic supports versus (b) metal catalysis inside an organic polymer framework (see text). R and P denote a reagent molecule migrating from the bulk of the solution to the metal nanocluster surface and a diffusing product molecule, respectively.

For MA materials, a perfectly detectable (scanning electron microscopy) micrometre-level porosity, called macroporosity, is observed already in the dry state (figure 2). The swelling phenomenon mainly produces the swelling of external layers, more or less thin, of the dense nodules that MA comprises (Guyot 1988), the surface of which represents the permanent pores of the MA materials themselves.

For GT materials, no porosity is detectable by electronic microscopies in the solid (dry) state, but scattered results reported in the literature (Hanson et al. 1974; Laufer & Hoelderich 2002) and quite recently systematically confirmed in our laboratories (see 3) do reveal, on indirect bases, that small nanopores must also exist in dry MA materials.

(c) Metalation of $\mathbf{P}$-F$s$ (production of $\mathbf{M}^n$/CFP materials)

The classic reactions involving $\mathbf{P}$-F materials are summarized in scheme 3. Equilibrium 1 is of fundamental importance in the so-called cation exchange process (Dorfner 1991). Reaction 2 is also relevant to the classic anion exchange practice and the chosen example is also relevant to the recently established, quite innovative process Acetica (Chiyoda Corporation; Corain et al. 2004b), a heterogeneous alternative to the homogeneous Monsanto process for the industrial synthesis of acetic acid. This process is based on a catalyst such as $\mathbf{P}$-NR$_4^+\text{[Rh(CO)$_2$I$_2$]}^-$ (Corain et al. 2004b), which is able to withstand working conditions that are not particularly mild. Reaction 3 is the access to a plethora of hybrid-phase metal catalysts (Corain et al. 2004b).
Figure 2. Schematic of the micro- and nanoscale morphology of (a) gel-type and (b) macroreticular resins (Centomo et al. 2009). Level 1 is the representation of the dry materials. Level 2 is the representation of the microporous swollen materials at the same linear scale: swelling involves the whole polymeric mass in the gel-type resin (2a) and the macropore walls in the macroreticular resin (2b). The morphology of the swollen polymer mass is similar in both gel-type and macroreticular resins (3a and b). Nanopores are actually formed by the void space surrounding the polymeric chains, as shown in level 4, and are a few nanometres wide (reproduced with permission from Corain et al. (2004a)).

For F=-SO₃H (e.g.)

\[
P₂SO₃H + M^{n+}/n \rightarrow P₂SO₃M^{n+}/n + H^+ \tag{1}
\]

For F = NR₄⁺ (e.g.)

\[
P₂NR₄⁺X⁻ + M⁻ \rightarrow P₂NR₄M⁻ + X⁻ \quad (\text{e.g. } M⁻ = \text{Rh(CO)}₂I₂) \tag{2}
\]

For F = generic Lewis base and ML'ₙ = generic metal co-ordination compound

\[
P₂F + ML'ₙ \rightarrow P₂F-ML'ₙ \tag{3}
\]

Scheme 3. Typical reactions involved in the metalation of \(P₂F\) materials.
3. Production and dispersion of metal (0) nanoclusters

As apparent from the literature, the predominant method to prepare $\text{M}_0/\text{Pd}$ materials is generally the so-called top-down approach (Kreibig et al. 2001)

$$\text{Pd}-\text{F-ML}_n \rightarrow \text{M}_0/\text{Pd}\text{-F}.$$ 

The metal centres are reduced by a variety of reductants to individual metal atoms that undergo a more or less rapid extensive aggregation to nano- and micro-aggregates that remain trapped inside the (normally) solvent-swollen polymer framework. In the case of GT resins, the nanoporosity of the swollen support is able to affect the size of the formed metal nanoclusters effectively (Corain et al. 2004a). A totally different (in experimental terms) approach, but not so far in conceptual terms, is the condensation of metal vapours onto the desired support (Vitulli et al. 2008). According to some literature reports (Hanson et al. 1974; Tibbitt et al. 1975), which were recently confirmed in our laboratories, $\text{Pd}$-F-bound metal centres can be reduced by di-hydrogen in the (dry) non-swollen state not only in metalated macroreticular but also in GT resins.

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**Figure 4.** Model for the generation of size-controlled metal nanoparticles inside metallated resins. (a) Pd$^{II}$ is homogeneously dispersed inside the polymer framework; (b) Pd$^{II}$ is reduced to Pd$^{0}$; (c) Pd$^{0}$ atoms start to aggregate in subnanoclusters; (d) a single 3 nm nanocluster is formed and ‘blocked’ inside the largest mesh present in that ‘slice’ of polymer framework, see text (reproduced with permission from Corain et al. (2004a)). Scale bar, 3 nm.

(a) **Evaluation of the physical (spatial) dispersion of metal nanoclusters inside the particles of $M^0$/CFP materials**

When evaluated in terms of chemical processing, each metalated bead of a $M^0$/CFP catalyst should be considered as a minireactor (figure 1) and the issue of the transportation of reagents and products might become a dominant one in terms of chemical productivity.

Mass transport depends very much on the micro- and nanoporosity of the swollen polymer frameworks in a given swelling medium, and in its turn this depends (especially in GT resins) on the mutual compatibility of the polymer chains with the swelling agent. Thus, if the metal nanoclusters do occupy the whole of the body of the microreactor, the circumstance might be an advantageous one in that the whole of the body of the microreactor and, in principle, all individual metal nanoclusters might participate in the catalytic action.

A convenient and practical tool for evaluating the dispersion of MNs in the body of the beaded support is the X-ray microprobe analysis of equatorial sections of the catalytic material’s particles (figure 3; Corain & Kralik 2001)
The issue of $M^0$ nanoclusters' size control

In the extensive world of $M^0/S$ catalytic materials, the problem of controlling the size of metal nanoclusters has been faced by means of a variety of synthetic routes (Bönnemann & Nagabhushana 2008).

We have discovered (Corain et al. 2004a) that the employment of GT resins featured by controlled polymer chain concentrations (Jeřábek 1985a,b), i.e. by a given nanoporosity in a given swelling medium, permits the isolation of size-controlled metal nanoclusters. The rationale that led to this discovery is illustrated in figure 4. We have gathered in at least four cases of evidence that
the size of a metal nanocluster produced inside, for example, a unit of volume of for example, $10 \times 10 \times 3 \text{ nm}$ is rationally conditioned by the size of the largest mesh existing in that volume unit.

It is important to stress that this nice correlation is valid for GT frameworks, while, for macroreticular ones, relatively large (tens to hundreds of nanometres in diameter) MNs (i.e. those generated inside the resin macropores) are also seen to co-exist with 2–4 nm ones, i.e. those generated in the nanoporous layer existing in the walls of the macropores themselves (Guyot 1988; D'Archivio et al. 2000; figure 5).

4. Catalytic behaviour of $\text{M}^0/\text{CFR}$ nanocomposites

For thorough accounts on this topic, the reader is referred to the papers published by Zecca et al. (2008), Centomo et al. (2009), Biffis et al. (2002) and Burato et al. (2009). In this shorter dedicated review, we would like to focus on the works of Biffis et al. (2002) and Burato et al. (2009).

Distinguished features of the catalytic activity of $\text{M}^0/\text{CFPs}$ are the effective, highly chemoselective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone (Biffis et al. 2002) and the fairly chemoselective hydrogenation of dihydrogen to hydrogen peroxide (Burato et al. 2009) under batch reactor conditions.

The chemoselective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone is a particularly challenging reaction, in that over-reduction to water is hard to prevent. Successful activity and chemoselectivity were achieved upon using a $\text{Pd}^0/\text{CFP}$ catalyst, in which the very marked lipophilicity of a poly-dodecylmethacrylate matrix was expected to provoke the expulsion of the less lipophilic product 2-ethylhydroanthraquinone from the body of $\text{Pd}^0/\text{CFP}$, thus contrasting the hydrogenation catalytic action of $\text{Pd}^0$ nanoclusters on the rings of 2-ethylanthrahydroquinone.

The fairly chemoselective (70% at 50% conversion) direct synthesis of hydrogen peroxide in the absence of any selectivity enhancers appears to be another successful and promising result of the use of an organic support (resin Bayer K2621) to produce a $\text{Pd}^0/\text{CFP}$ catalyst.

As to the potential uniqueness of $\text{M}^0/\text{CFP}$ catalysts, an emblematic case is the behaviour described by Wissler et al. (2007; see table 1), in which the authors point out (and stress the point) that the success of the complex reaction sequences leading to the multi-functional final product is due to the successful intervention of a $\text{Pd}^0/\text{CFP}$ catalyst ($\text{Pd}^0$/Amberlyst-15), while a number of traditional catalysts turned out to be totally inactive.

5. Conclusions

Metal–resin nanocomposites based on a nanostructured metal (0) component and functional resins can be easily prepared and thoroughly characterized as potential catalysts in a variety of useful synthetic reactions. $\text{M}^0$–resin nanocomposites are cheap materials that might be irreplaceable catalysts in complex multi-step syntheses.
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