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2012

# Synthesis of supported metal nanoparticle catalysts using ligand assisted methods

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NANOSCALE, CAMBRIDGE, v. 4, n. 19, pp. 5826-5834, FEB, 2012

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Cite this: *Nanoscale*, 2012, **4**, 5826

www.rsc.org/nanoscale

## FEATURE ARTICLE

**Synthesis of supported metal nanoparticle catalysts using ligand assisted methods**

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Received 11th May 2012, Accepted 23rd July 2012

DOI: 10.1039/c2nr31165h

The synthesis and characterization methods of metal nanoparticles (NPs) have advanced greatly in the last few decades, allowing an increasing understanding of structure–property–performance relationships. However, the role played by the ligands used as stabilizers for metal NPs synthesis or for NPs immobilization on solid supports has been underestimated. Here, we highlight some recent progress in the preparation of supported metal NPs with the assistance of ligands in solution or grafted on solid supports, a modified deposition–reduction method, with special attention to the effects on NPs size, metal–support interactions and, more importantly, catalytic activities. After presenting the general strategies in metal NP synthesis assisted by ligands grafted on solid supports, we highlight some recent progress in the deposition of pre-formed colloidal NPs on functionalized solids. Another important aspect that will be reviewed is related to the separation and recovery of NPs. Finally, we will outline our personal understanding and perspectives on the use of supported metal NPs prepared through ligand-assisted methods.

**1. Introduction**

Heterogeneous catalysis has received a great deal of attention with the advent of nanoscience due to advances in

characterization techniques and preparation methodologies of metal nanoparticles (NPs). Aberration-corrected environmental transmission electron microscopy has been recently used to understand how molecules can restructure the surfaces of heterogeneous catalysts under reaction conditions.<sup>1</sup> It was shown by using this technique that adsorbed carbon monoxide molecules caused the {100} facets of gold NPs to reconstruct during

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*the synthesis of supported metal nanoparticles with controlled sizes and morphologies for applications in the field of catalysis, and the development of magnetically recoverable catalysts to facilitate catalyst recovery and recycling in liquid phase reactions.*

CO oxidation at room temperature. The CO molecules adsorbed at the on-top sites of gold atoms in the reconstructed surface, and not only onto low-coordination sites such as steps, edges, and corners as postulated before. New synthesis techniques promise to achieve a better control of composition, size, morphology, and surface properties of metal NPs with respect to traditional techniques used for the preparation of heterogeneous catalysts, such as deposition–precipitation. This high degree of control enables systematic studies of the influence of composition and structural features of monodispersed metal nanoparticles on chemical reactivity and selectivity, leading to an increasing understanding of relationships between structure and catalytic activity and the design of more efficient catalysts.<sup>2–8</sup>

The reduction of metal particles size to the nanoscale has consequences, such as the increase of the surface-to-volume ratio and thus the number of catalytic active sites, which maximizes the use of noble metals. However, the catalytic activity is not dependent only on the particle size, and maximum activity at a certain optimal intermediate size has been reported,<sup>9–11</sup> which suggests that both the number of surface metal atoms (active sites) and the electronic properties at nanoscale can have a profound impact on catalytic activities.

Metal NPs have low stability against agglomeration, since the bulk metal is the thermodynamic minimum, and therefore organic ligands, surfactants, polymers or inorganic coatings are employed to stop the particle growth process, control the size of NPs and keep them stable by steric or electrostatic stabilization.<sup>12–14</sup> The stabilization of NPs in the same phase as the reactants might hamper the separation of the catalyst. Strategies to facilitate NPs separation include decantation by using biphasic systems, such as the biphasic system water/organic solvent<sup>15–17</sup> or the two-phase system with ionic liquids,<sup>18–20</sup> and filtration or centrifugation by the immobilization of NPs on organic or inorganic supports (magnetic decantation can be used with magnetic supports<sup>21</sup>). In general, NP catalysts supported on solids exhibit higher catalytic activities than the same NPs applied in biphasic systems.<sup>22,23</sup>

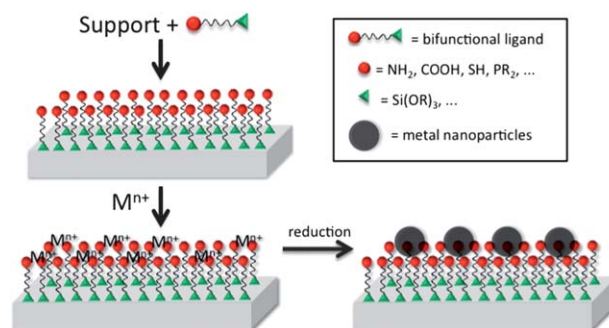
Supported metal NPs can be prepared by means of methodologies where the particle size and size distribution are finely controlled and can be used for both liquid-phase and gas-phase reactions. However, the presence of protective organic capping ligands or their decomposition products is mainly considered to have a detrimental effect on catalytic activity as they can block catalytically active sites on the nanoparticle surface.<sup>24,25</sup> The organic ligands are suggested to be carefully selected (weakly bound ligands are preferred) or even removed to recover activity. Nevertheless, the capping ligands can also act as spacers between the metal NPs and the support in such a way that beneficial metal–support interactions can be obtained, tuned and optimized in order to increase the activity of supported metal catalysts.<sup>26</sup> Additionally, the capping ligands can create micro-environments on NP surfaces and affect reaction selectivity, presumably, by preventing binding of the substrates to certain sites on the NP surface. Besides the ligands used in synthetic protocols as stabilizers for NPs, new functional groups can be anchored on the solid support to assemble NPs, a very well known strategy in other fields of application.<sup>27</sup> When a functionalized solid is exposed to a solution of NPs, the terminal groups enhance the metal–support interaction and attract the

metal NPs onto the surface of the solid. Two ligands of widespread use are dithiols on gold<sup>28</sup> and organoalkoxysilanes on silica.<sup>29,30</sup> In catalytic applications, however, those ligands grafted on the support surface can affect the catalytic properties of the supported metal NPs, but this possible influence has been underestimated until recently.

In this feature article, we summarize some of the emerging approaches for the preparation of supported metal NPs with control of the variables affecting catalyst activity and selectivity, such as size, size distribution and surface properties, with special attention to modified methods with the assistance of ligands in solution or anchored on the solid support. It is important to mention that the understanding on how the ligands influence NPs morphology, metal–support interactions and catalytic activities is still very low. After a discussion on the general strategies in metal NP synthesis assisted by ligands grafted on the solid support – a modified metal deposition and reduction method (Fig. 1), we highlight some recent progress in the synthesis of supported metal NP catalysts by deposition of pre-formed colloidal NPs.

## 2. Metal deposition and reduction on functionalized solid supports

Heterogeneous catalysts are typically prepared by the succession of deposition, drying, calcination, and activation steps.<sup>31</sup> The deposition process can be as simple as wetness impregnation, however, it can be improved by adjusting process parameters such as concentration, pH, solvent, temperature, metal precursors, reducing agents, *etc.*<sup>32</sup> All these parameters can be changed to improve the quality of the final catalysts, but a precise control of particle size and morphology is difficult to achieve. A parameter that is less explored, although it can improve the traditional methods to produce heterogeneous catalysts, is the functionalization of the support surfaces with organic modifiers. The presence of organic ligands can limit the temperature of operation of the final catalyst, because they can decompose upon heating, but there are also many advantages associated with the introduction of binding sites on the solid support. Catalyst supports like silica and other oxides can be chemically modified by many commercially available organoalkoxysilanes, and many other derived groups can be prepared, as for example, by preparing Schiff-bases from 3-aminopropyl-functionalized silica,



**Fig. 1** Schematic representation of the ligand assisted method for the preparation of supported metal NPs.

by means of simple synthetic strategies. Various other types of functionalization of silica with ligands are known, as for example, P, N ligands constituted with bisphosphinoamino moiety, diphenylphosphino pyridine moiety, dendrimers, alkylimidazolium ionic liquids, to say some. Those groups can be selected and used to improve metal precursor impregnation rates, to improve metal-support interaction, to avoid metal leaching into the liquid phase and to control particle aggregation and growth.

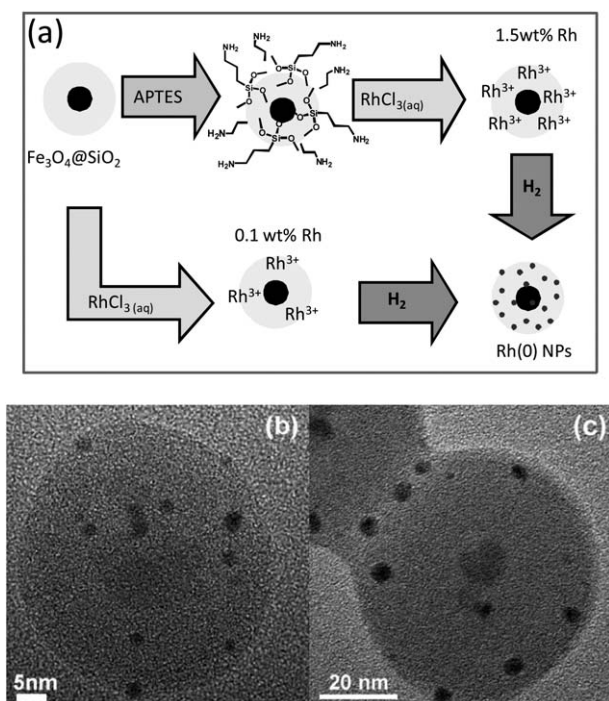
We investigated the ability of silica functionalized with amino groups, obtained by reaction of the silica surface with 3-aminopropyltriethoxysilane, to be impregnated with metal precursors for the synthesis of NPs. In several examples studied, the amount of metal ions loaded on the support was always higher in the functionalized silica by at least 10 times the amount loaded on non-functionalized silica. This behavior was observed for Rh(III),<sup>33</sup> Pt(II),<sup>34</sup> and Ir(III) salts.<sup>35</sup> The metallic precursors loaded on the solids were reduced with hydrogen resulting in nearly 2–5 nm supported metal NPs (Fig. 2).

The Rh NPs supported on amino-functionalized silica were very active and stable catalysts for successive hydrogenation reactions of cyclohexene, while converting up to 180 000 mol<sub>substrate</sub>/mol<sub>catalyst</sub> (TOF up to 40 000 h<sup>-1</sup>), as well as for the hydrogenation of benzene, while converting up to 11 550 mol<sub>substrate</sub>/mol<sub>catalyst</sub> (TOF up to 1100 h<sup>-1</sup>) under mild conditions. The reactions were performed in the liquid-phase with negligible metal leaching to the products, which suggests a high efficiency of catalyst separation and the strong metal-support interaction.<sup>33</sup> The catalysts were also tested with polar substrates

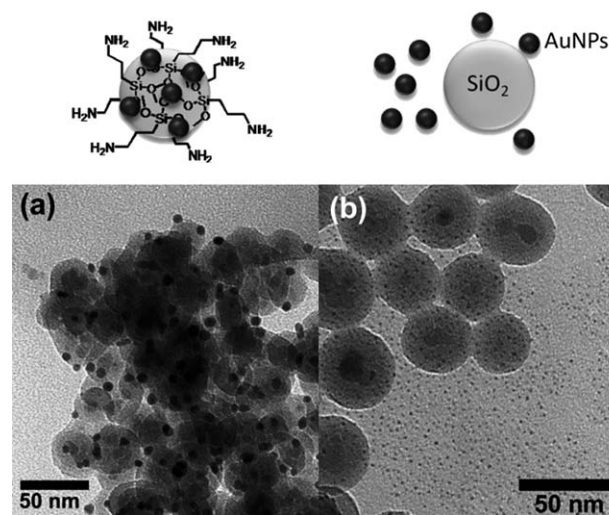
and the one prepared with the non-functionalized silica has shown at least 100 times more metal leaching than the catalyst prepared with amino-functionalized silica.<sup>35</sup>

Impregnation studies with gold ions have shown very low affinity of gold(III) ions to silica surfaces, but an enhanced interaction was obtained by coordination of gold ions to amino groups of functionalized silica surfaces.<sup>36</sup> Non-functionalized and amino-functionalized silica supports were loaded with Au<sup>3+</sup> precursor and the intermediate species were characterized by X-ray absorption near-edge spectroscopy (XANES). The non-functionalized solid was prepared by wetness impregnation in such a way that both solids were loaded with the same amount of gold. The comparison of XANES spectra obtained from the material with and without functionalization, and the standards Au<sup>0</sup> and Au<sup>3+</sup> have shown that the white line intensity of gold loaded on amino-functionalized silica decreased relative to the Au<sup>3+</sup> standard, indicating a partial reduction of the gold ions. This behavior indicated that there was a strong interaction between the amino groups and the gold ion thus causing a change in coordination environment and oxidation state of the metal. In the case of the non-functionalized support, there was an intermediate white line intensity, which suggests a weak interaction with the oxygenated species on silica surfaces. After reduction of gold, the non-functionalized support contains NPs that were not attached to the support, indicating the weak interaction with the silanol groups. In the case of the amino-functionalized support, the NPs formed were exclusively deposited on the support (Fig. 3).<sup>36</sup>

Studies on the mechanism of formation of supported metal NPs have been reported,<sup>37</sup> but the influence of the ligands on the kinetics of metal NPs formation was not well elucidated yet. In the preparation of supported metal NPs by deposition and reduction of metals on functionalized solid supports we can expect the coordination of the metal ions to the ligands grafted on the support surface, and consequently a direct influence in the reduction step and particles' growth process.



**Fig. 2** (a) Schematic representation of ligand assisted preparation of supported Rh NPs, (b) TEM of Pt NPs supported on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>NH<sub>2</sub> (reprinted with permission from ref. 34 (Copyright 2009 Elsevier)) and (c) TEM of Rh NPs supported on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>NH<sub>2</sub> (reprinted with permission from ref. 33 (Copyright 2008 Elsevier)).



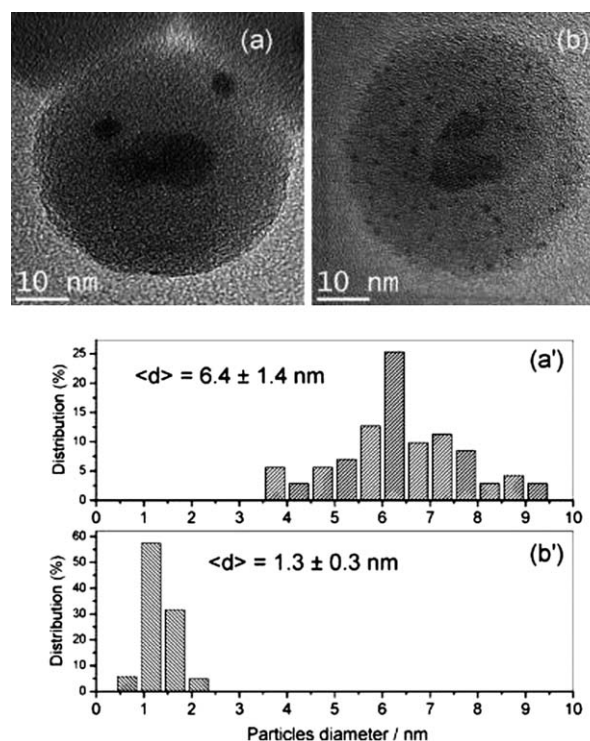
**Fig. 3** TEM images of gold NPs supported on (a) amino-functionalized and (b) non-functionalized silica. Reprinted with permission from ref. 36 (Copyright 2011 John Wiley and Sons).



## 2.1. Particle size tuning

The preparation of soluble metal NPs involves primarily chemical methods, which result in good control of the shape, size and size dispersion by simply choosing the amount and nature of stabilizers.<sup>9–12,38–40</sup> However, achieving size control during the preparation of supported metal NPs, which have great importance for use in catalysis due to the easy separation from the reaction medium and high stability against agglomeration, is not trivial. A strategy that has received great attention is the immobilization of pre-formed NPs on solid supports (discussed later). In this section we will discuss strategies for obtaining size controlled supported metal NPs prepared by reduction of metallic precursors impregnated on solid supports (wetness or wet impregnation). The attempt to control NP size is usually done by varying the metal loading,<sup>41,42</sup> or using nanoporous materials as templates for the formation of NPs within the pores.<sup>43</sup> The introduction of ligands within the pores of nanostructured materials has been used as a strategy to control the growth of nanoparticles exclusively in the pores of the host matrix.<sup>44</sup>

Considering the difficulty of preparing supported NPs of uniform size and also selecting the desired size range, we made several contributions to this field by presenting a new method that includes the modification of the support surface with different functional groups.<sup>45</sup> This very simple strategy allowed the formation of NPs of differing sizes by changing functional groups on silica surfaces. Silica surfaces were functionalized with amino and ethylenediamino groups by reaction with organoalkoxysilanes and then impregnated with the same amount of Pd<sup>2+</sup> ions. After metal reduction with hydrogen under mild conditions, supported palladium NPs of 6.4 and 1 nm were obtained, respectively (Fig. 4). Additionally, the non-functionalized support was loaded with Pd<sup>2+</sup> ions and after reduction it lead to the formation of metal aggregates and little dispersion of the solid throughout. The way how different ligands can affect the size of the NPs formed is certainly related to the complexes formed between the metal and the ligands grafted on the surface of the support and the influence of these complexes formed on the NPs growth step. The supported Pd NPs catalyze the hydrogenation of cyclohexene to cyclohexane at turnover numbers of 2500 mol<sub>substrate</sub> per mol<sub>catalyst</sub> in 187 min (ethylenediamine) and 27 min (amine), which correspond to turnover frequencies (TOF) of 800 h<sup>-1</sup> and 5500 h<sup>-1</sup>, respectively, using the total amount of metal. The smaller NPs (*ca.* 1 nm) are less active and less suitable to catalyze the hydrogenation reaction than the larger NPs (*ca.* 6 nm). The effect of the NPs size on catalytic activity has been extensively studied<sup>9,10,46–48</sup> and, unlike expected, reducing the size of NPs does not necessarily represent an increase in reaction rates. The catalytic activity can be influenced by electronic or geometric effects, such as the presence of surface low coordination number atoms, size-dependent metal–ligand binding energies, distortions of the crystal structure, different types of facets, the presence of corners, and interactions with the support. In order to check their stability, the catalysts were used in successive hydrogenation reactions. Pd catalysts prepared on the non-functionalized and amino-functionalized supports were reused 20 times by adding new portions of cyclohexene to the recovered solid. The non-functionalized



**Fig. 4** Micrographs of palladium NPs of 6 and 1 nm supported on a solid type core–shell silica-coated magnetite functionalized with (a) amine and (b) ethylenediamine groups. Reprinted with permission from ref. 45 (Copyright 2009 American Chemical Society).

catalyst lost activity upon recycling and the amino-functionalized catalyst showed no significant change in catalytic activity during the first 20 reuses. Since metal leaching was negligible in both systems, the loss of activity observed in the non-functionalized support suggests aggregation of metal particles that is less probable to occur when the particles are stabilized by the amino groups on the support surface. The catalyst prepared on the ethylenediamine-functionalized support was completely deactivated after the fourth reuse. The small size particles appear to have been poisoned, which can be suggested as a consequence of the higher affinity of small curved particles for ligands, so that they are not able to dissociate as required to maintain the catalytic activity.<sup>49</sup>

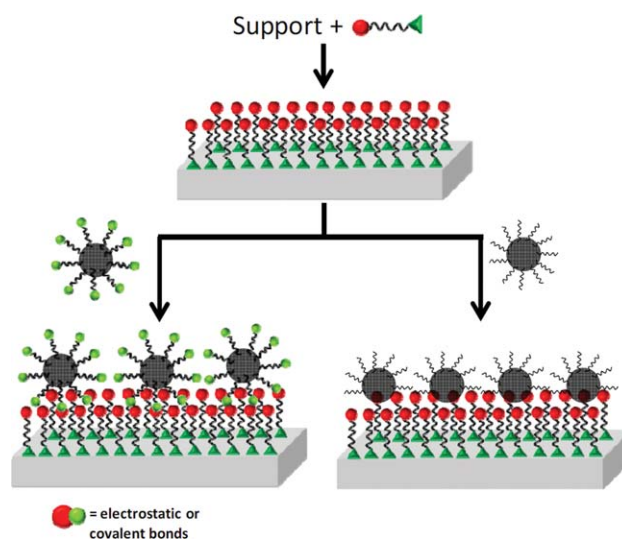
## 3. Deposition of pre-formed metal nanoparticles on solid supports

The deposition of pre-formed metal NPs on a support has become a preferred methodology to prepare supported nanocatalysts, because it promises a much higher control over the particle size and morphology.<sup>4</sup> The NPs synthesis and the deposition on the support are separated into two subsequent steps, and considering that particle sizes usually do not change during the deposition process, the size control of NPs that is achieved by selecting the method of synthesis of the colloidal NPs is transferred to the supported NPs. The morphology, the size and the dispersion of the NPs obtained by this two-step methodology are extremely important for their behavior as catalysts.<sup>50–53</sup>

The metal NPs can be prepared by well known synthetic methods, such as chemical methods *via* chemical or electrochemical reduction and thermal decomposition of salt precursors. The selection of the preparation method by changing the metal precursor (metal salts or organometallic compounds), reducing agent, stabilizing agent and solvent determines the conditions for nucleation and growth of NPs to the desired shape and size. The ligands present in solution promote the stabilization, direct the morphology and define the size and dispersion of the metal NPs. However, the surface properties of pre-formed NPs (hydrophobic or hydrophilic) and possible weak metal–support interaction may result in leaching of metal during catalytic reactions. We have experienced metal leaching problems when using toluene as a solvent in a system prepared by deposition of gold NPs on a silica-based support, and the change to a more polar solvent resulted in a very active gold catalyst for the oxidative esterification of alcohols.<sup>50</sup>

The deposition of the colloidal NPs on solid supports, usually SiO<sub>2</sub>, TiO<sub>2</sub> and C prepared by different procedures and having different surface areas and morphologies, can be accomplished by many procedures recently reviewed by Jia and Schüth.<sup>3</sup> The authors discussed five variations of deposition methods for colloidal NPs on solid supports, *i.e.* the direct colloidal deposition, colloidal deposition by surface modification, colloidal deposition by ion-exchange, colloidal deposition using flame spraying techniques and finally, colloidal deposition using Langmuir–Blodgett. Another technique for colloidal metal NPs deposition that deserves attention is the dry impregnation in fluidized bed explored by Barthe *et al.*<sup>54,55</sup> This technique consists in spraying a solution containing the metal source into a hot fluidized bed of porous support. A catalyst prepared by deposition of colloidal Rh NPs on porous silica particles using this very method was very active for hydrogenation of aromatic compounds under mild conditions. Additionally, this technique preserves the NPs morphology and size, and avoids loss of metal in the impregnation process.

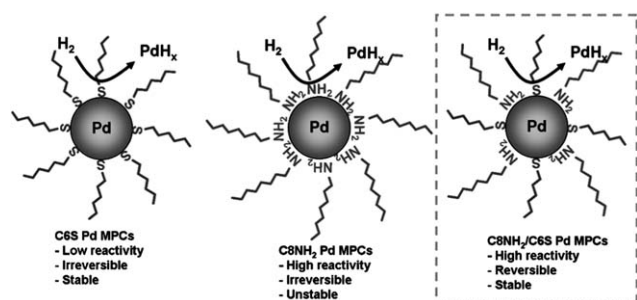
The deposition of colloidal metal NPs on solid supports, similar to the well known wet impregnation method used for metal salts, may not be so effective, because the surfaces of the metal NPs are usually modified with organic ligands and electrostatic interactions are drastically suppressed. Depending on the electrical charges on the support surface (and NPs), the support repels the particles in solution instead of attracting them toward it. The electrical charges on the support surface and NPs can be changed, for example, by adjusting the pH of the impregnation aqueous solution and in some particular situation negatively charged metal NPs are easily deposited on the positively charged support by electrostatic attraction.<sup>56</sup> The colloidal deposition by the surface modification method (Fig. 5) uses the principle that modification of the support and NP surfaces with complementary ligands (neutral or charged ligands) will improve the linkage of the NPs to the support. Ligands with various linkage capabilities can be readily introduced either to the surface of the support (as for example by means of organoalkoxysilanes in silica) or to the metal NPs. Gold NPs were nicely supported on silica by an electrostatic assembly of amino-modified silica spheres and citrate-coated gold NPs.<sup>57</sup> Other examples of electrostatically and covalently bonded metal–support assemblies are given in the same reference. The nature of



**Fig. 5** Schematic representation of colloidal deposition by the surface modification method.

the bonding between the NPs and the support determines the stability and dynamic of the supported NPs and, in principle, the strength and nature of the bonds can be tailored. The coordination capture method (Fig. 5) is a modification of the method described above and is based on the functionalization of the support with strong coordinating ligands and the impregnation of NPs synthesized with weak coordinating groups (for example, poly(vinyl-pyrrolidone) (PVP)). The NPs will be captured due to ligand affinity with the functionalized support. Khatri *et al.*<sup>58</sup> studied the deposition of ionic liquid-stabilized gold NPs on 3-mercaptopropyl-functionalized silica. The authors observed that the weakly coordinated ionic liquid molecules could be, to some extent, replaced with thiol groups of the functionalized support. The Au–S chemisorption linkage resulted in strong immobilization of the Au NPs. Some of the Au NPs are supported by physisorption and detach from the silicon surface upon treatment with 1-dodecanethiol.

In order to better understand the influence of surface ligands on catalytic activities, we performed an experiment where palladium NPs were synthesized in solution and the pre-formed Pd NPs were deposited on silica supports functionalized with amino and ethylenediamino groups (unpublished results). A great influence on the reaction rates depending on the functional group grafted on the surface of the support was observed, even though the support contains PVP stabilized Pd NPs of the same size. The catalytic properties of the Pd NPs supported on functionalized solids were compared using the solventless hydrogenation of cyclohexene as a model reaction. The catalytic activity of the catalyst supported on amino-functionalized silica (TOF = 50 000 h<sup>-1</sup>) is 25 times higher than the catalyst supported on ethylenediamino-functionalized silica (TOF = 2000 h<sup>-1</sup>). Therefore, the only reasonable explanation for the marked difference of catalytic activity is the influence of the ligands grafted on the support surfaces. The ethylenediamine ligand has a strong deactivating effect on the activity of the Pd NPs suggesting a preferential interaction with the active sites of the Pd NPs when compared with amine groups. These results demonstrate that the same challenges for catalytic applications of



**Fig. 6** Schematic representation of H<sub>2</sub> interaction with Pd colloidal NPs stabilized by alkyl thiols and alkyl amines. Reprinted with permission from ref. 61 (Copyright 2011 American Chemical Society).

colloidal NPs, also called “soluble nanoparticles”, exist for supported NPs. Undoubtedly the deposition of pre-formed colloidal NPs on a support is an excellent method to prepare supported metal NPs of controlled size and shape. The same control is usually not possible by direct deposition of metal salts followed by reduction. However, the organic molecules, polymers and surfactants that are necessary to control the particles growth and protect them against agglomeration may also block the active sites for surface catalysis. Stowell and Korgel<sup>25</sup> described the catalytic activity of Ir NPs prepared with different capping ligands. They have shown that the catalysts prepared with strong coordinating ligands contain high quality monodispersed NPs, but are inactive for hydrogenation of decene, while the catalysts prepared with weak coordinating ligands, which contain NPs with broader size distribution, are very active. Similarly, the activity of gold catalysts is detrimentally affected when strong coordinating ligands (*i.e.* alkanethiols) are added to pre-formed catalysts.<sup>59</sup> Nonetheless, Au NPs prepared using two weakly coordinating nitrogen-based capping ligands, poly(vinylpyrrolidone) (PVP) and dodecylamine (DDA), showed distinct catalytic activity.<sup>60</sup> The authors suggested that the weakly bound capping ligands may induce diffusion limitations and lower the accessibility to the active sites. PVP-based polycrystalline NPs compensate the negative effect of diffusional hindrance and are more catalytically active than the DDA-based single-crystal NPs. Moreno *et al.*<sup>61</sup> showed a differing behavior of Pd NPs capped with octylamines and hexanethiolates in the presence of H<sub>2</sub>. While the NPs capped with octylamines showed high reactivity and low stability, the Pd NPs capped with hexanethiolates presented opposite behavior, but both were irreversible after H<sub>2</sub> exposure. When these Pd NPs are stabilized by both ligands the particles showed high reactivity, stability and reversible behavior (Fig. 6). Therefore, the selection of the capping ligands for colloidal NPs synthesis is an import step since weak or strong coordination groups, which will interact differently with the metal surfaces, can alter the behavior of the NPs as catalysts. A compromise between NPs quality and catalytic activity is always a concern. Removal of capping ligands by post-synthesis protocols is an alternative to restore the catalytic activity of NPs.

### 3.1. Catalytic activity without removing stabilizing agents

The impregnation of colloidal NPs on a solid support followed by washing steps without any additional treatment to remove stabilizing agents allows the formation of very active catalysts.<sup>23</sup>

Roucoux groups have described many examples of colloidal Rh NPs synthesized in the aqueous phase in the presence of the surfactants and then impregnated on different supports. The supported Rh NPs are very active catalysts in the hydrogenation of aromatics compounds.<sup>62–64</sup>

Lopez-Sanchez *et al.*<sup>65</sup> investigated the effect of catalyst preparation on the activity of AuPd supported NPs. Carbon supported AuPd NPs were synthesized by impregnating metal precursors and colloidal NPs (sol deposition method), and the catalytic activities were compared in the oxidation of benzyl alcohol. The sol-immobilized 1 wt% (AuPd)/C catalysts are more active by a factor of 8–12 than the 5 wt% (AuPd)/C synthesized by the impregnation method. In the same paper, the sol-immobilization of AuPd NPs on TiO<sub>2</sub> was investigated and tested in CO oxidation and hydrogen peroxide synthesis. For CO oxidation, the supported colloidal catalysts need to be activated by thermal treatment to partially remove protective stabilizing ligands. Bäumer *et al.*<sup>66,67</sup> showed that molecules like CO can penetrate a ligand shell and that catalysts obtained from ligand-stabilized nanoparticles can be directly used as CO oxidation catalysts without any pretreatment.

### 3.2. Catalytic activity by removing stabilizing agents

A calcination step after impregnation of colloidal NPs on a solid support can help to remove the capping ligands and to recover the catalytic activity.<sup>68</sup> However, calcination can compromise the dispersion of the NPs on the support because of NPs aggregation, sintering, or size and morphology changes compared to the initial colloidal synthesis. In some cases, the temperature causes decomposition of the organic ligands forming carbonaceous deposits that have to be removed through oxidation–reduction cycles.<sup>69</sup> Sellin *et al.*<sup>70</sup> studied the thermal stability of Pt colloidal NPs prepared in the presence of tetraalkylammonium triethylborohydride and then impregnated on a carbon support. The particles size change was analyzed before and after calcination, clearly showing aggregation. Moreover, the X-ray diffraction peaks for the sample after calcination confirmed the increase of Pt crystallite size. It is also possible to find some examples where calcination has less aggregation effects allowing the synthesis of well-dispersed supported metal NPs.<sup>71</sup> The behavior of the supported colloidal NPs after calcination to remove stabilizing agents varies according to the methods used for catalysts synthesis.

Lopez-Sanchez *et al.*<sup>72</sup> suggested an efficient method to remove polyvinyl alcohol (PVA) from colloidal Au supported on TiO<sub>2</sub> that consists in refluxing the catalyst in water. With the aid of high-angle annular dark images field they showed that the water extraction procedure removes a substantial fraction of the stabilizing PVA molecules from the supported Au NPs, which does not increase significantly the particle size and does not affect their morphology, in contrast to that observed after calcination. The catalytic activity of the catalyst treated with hot water in the oxidation of CO was significantly higher than the calcined catalyst. This methodology can be an important approach to minimize the problem associated with the reduced catalytic activity of colloidal NPs related to the presence of stabilizing agents on metal surfaces.



The removal of ligands from the NPs surface can also be improved by the choice of the support. According to the Lewis acidity of the support it is possible to vary the degree of spillover effect. Wang *et al.*<sup>73</sup> showed that the high Lewis acidity of the support improved the degree of spillover of Pt NPs stabilized by dodecylamine. The consequence is that the higher the spillover effect the higher the catalytic activity in CO oxidation.

#### 4. Catalysts separation and recovery

Platinum group metals supported on carbon are among the most widely used catalysts in organic transformations. For example, the commercially available catalysts Pd/C, Rh/C and Pt/C show excellent catalytic activity in a wide range of organic reactions, especially hydrogenations, which are often used in laboratory and also in industry.<sup>74–77</sup> Considerable efforts have been made to increase the efficiency of catalytic systems through, for example, the choice of other solid supports with optimized surfaces, such as nanoporous carbon, carbon nanotubes and nanofibers. New strategies to the recovery and recycling of catalysts of platinum group metals are highly desirable and can result in significant economic and environmental benefits. The separation and recovery of supported metal NP catalysts can be greatly facilitated by using supports with magnetic properties. Our research group has used magnetic NPs as supports for catalysts of this type, especially to overcome the difficulty of filtering the finely particulate material. The magnetic separation is a powerful tool to facilitate separation of catalysts from the reaction and therefore offers an alternative to one of the most important problems in liquid phase catalysis – the separation of the catalyst and the desired recycling and reuse of catalysts. Unlike procedures such as filtration, centrifugation or extraction (or chromatographic techniques), the magnetic separation approach eliminates the use of auxiliary substances (solvents, filters, *etc.*) and prevents catalyst oxidation and loss of catalyst, making the process cleaner, environmentally safe and fast.

Pd NPs were formed directly on the surface of iron oxide NPs functionalized with 3-mercaptopropionic acid (3-MPA)<sup>78</sup> or magnetic NPs functionalized with organoalkoxysilanes. Pd catalysts were also prepared using magnetic iron oxide NPs coated with silica by the modified Stöber method<sup>79</sup> or by the microemulsion method that results in a core-shell structure silica-magnetite.<sup>33</sup> Metal catalysts with excellent catalytic properties in hydrogenation of olefins, higher than Pd/C, with the advantage of being fully recovered at the end of the reactions by the simple use of a permanent magnet and reused in subsequent reactions, were prepared successfully. Metal NPs of Pd,<sup>45</sup> Rh,<sup>33</sup> Pt,<sup>34</sup> Ir,<sup>35</sup> and Ru<sup>80</sup> showed excellent catalytic activities in hydrogenation reactions. The Rh NP catalyst was used in hydrogenation reactions of polyaromatic compounds with complete conversion of anthracene in hydrogenated products under mild reaction conditions.<sup>81</sup> Magnetically recoverable Au NPs with excellent properties for oxidation reactions were also prepared.<sup>36,82</sup>

#### 5. Conclusions and outlook

Controlling the size and size distribution of supported metal NPs for catalytic applications is much desired. Most heterogeneous

catalysts are synthesized with less control on particles size and size distribution range than colloidal NPs, thus it is possible that only a small portion of the metal is in the most active size and is responsible for the observed activity. Understanding the fundamental aspects of catalysis by NPs, such as correlations between the structure and activity, is possible only when the preparation techniques allow obtaining high quality and well-characterized nanomaterials. Concurrent with the synthesis of new nanoparticle based catalysts, however, a number of important issues require further examination. These issues include catalyst formation mechanism, catalyst stability, metal leaching, catalyst lifetime, and deactivation mechanisms. Moreover, the comprehension of how these properties are affected by the ligands used as stabilizers for the metal NPs synthesis or for NPs immobilization on solid supports is of crucial importance. The organic capping ligands are mainly considered to have a detrimental effect on catalytic activity as they can block catalytically active sites on the nanoparticle surface. However, they can create unique environments on the NP surface that influence activity and selectivity, presumably, by preventing binding of the substrates to certain sites on the NP surface. If one is able to finely tune the properties of the NP surfaces, for example, either by creating hydrophobic/hydrophilic surfaces or by changing the local pH on the surface near to the reactive sites to a different value than the bulk solution, very interesting reactivities could be achieved. The role of the capping ligands in the performance of metal NP catalysts has been underestimated until recently, when stabilizers were suggested to improve the activity, selectivity, stability, solubility and recyclability of metal NPs.

In recent years we have studied methods of reduction and the role of functionalizing supports in the formation of size controlled and morphologically well-defined supported metal NPs. We finally concluded that not only the ligands used as NP stabilizers can affect catalytic activities, but also the ligands grafted on the solid support surfaces have caused changes in the catalytic performances of supported NPs. Moreover, the presence of functional groups on the surface of solid supports can contribute to: (i) control the size of NPs deposited on the support; (ii) improve the impregnation of metal precursors on the support; (iii) improve metal-support interaction avoiding metal leaching into the liquid phase; and (iv) affect the reactivity, either by size control or by other properties granted by the auxiliary ligands grafted on the solid support.

Despite the growing interest, NP catalysts have not yet found broad applications in complex molecule synthesis,<sup>83</sup> with most applications thus far limited to cross-couplings, oxidations and reductions. The introduction of chiral ligands that anchor robustly to the metal surface of NPs and resist displacement has been effective in directing truly heterogeneous enantioselective catalytic reactions,<sup>84</sup> but much more research is necessary in this field to broaden the scope of nanocatalysis to the very desired enantioselective reactions. In many examples, however, the NPs are merely metal reservoirs for the formation of active molecular catalytic species. In this respect, it should be mentioned that knowing whether the true catalyst is the NP metal surface, or actually molecular metal species, or even small sub-nanometer clusters, is crucial for any study. Close collaborations between heterogeneous catalysis, homogeneous catalysis, and kinetic and



theoretical studies might be beneficial in advancing this area of catalysis.

## Acknowledgements

The authors acknowledge support from FAPESP, CAPES, CNPq and INCT-Catalise.

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