Heterogeneous Catalysis

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Ligand Capping of Colloidally Synthesized Nanoparticles—A Way to Tune Metal–Support Interactions in Heterogeneous Gas-Phase Catalysis**

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Catalysis by noble metals is still extremely important for the industrial production of chemicals,[1] in catalytic converters,[2] and in new areas of energy generation (e.g. fuel cells[3]) and storage (e.g. batteries[4]). Since the supplies of these metals are limited and their prices continuously increase, the search for new classes of catalytic materials, such as cheap and abundant oxides,[5] and significant improvement of the performance of existing metal catalyst systems is indispensable.

An attractive option in this context is the use of the support as a co-catalyst; in other words, shifting the main task of the support from ensuring sufficient particle dispersion to participating in the catalytic cycle. Particularly interesting in this respect are so-called strong metal–support interactions (SMSI) which have been the subject of a number of catalytic studies since their discovery in the 1970s.[6] Many different transition-metal oxides, such as TiO_2,[7] CeO_2,[8] and WO_3[9] are known to show a SMSI effect which can strongly influence the electronic structure of metal catalysts and even lead to thin oxide layers covering the metal nanoparticles.[10] While in some cases (e.g. toluene hydrogenation on Pt/TiO_2[11]) the SMSI effect was found to decrease the overall catalytic activity (by diminishing the number of active sites through encapsulation of the metal particles by the oxide), in other cases it can considerably improve activity (e.g. CO oxidation on Pt/TiO_2[12]).

Such synergism can for instance result from the fact that the oxide provides special adsorption sites at the perimeter of the particles,[11] induces a different particle morphology,[7] or delivers active species.[12] Since CO oxidation on Pt, for instance, suffers from the fact that CO is strongly bound to Pt and thus poisons the surface so that O_2 cannot adsorb at low temperatures, a supply of oxygen by the support should improve the performance drastically. Indeed, this type of SMSI effect was recently observed:[13] The interaction of Pt with FeO, which delivers oxygen at the border between the two constituents, was exploited in the development of a very efficient catalyst for PROX (preferential oxidation of CO in the presence of hydrogen) which already works at room temperature. Besides the possible contribution of subsurface Fe,[14] the active site was discussed to be a highly reduced FeO layer on Pt, while hydrogen is necessary to replenish these reduced sites.[13]

Although the potential of SMSI is clear and industrial companies are already benefitting from such catalysts, rational concepts to generate and tune SMSI are still largely missing in the literature. One possible strategy is the use of supported preformed colloidal nanoparticles instead of metal precursors which are assembled into particles only in subsequent steps on the surface. Here, spacers between the catalytic particle and the support in the form of organic ligands can be employed which can possibly mediate the interaction between the metal and the support. Another great advantage of using colloidal nanoparticles is the structure control achieved in the colloidal synthesis, making it possible to optimize catalytic properties by steering particle size, morphology, and composition.[15]

Nevertheless, as in heterogeneous gas-phase catalysis, organic stabilizers are mainly considered to have a detrimental effect on catalytic activity,[16] a route using ligand-capped nanoparticles to obtain highly active catalysts seems contradictory at first. However, in previous publications we could show[17] that molecules like CO can penetrate a ligand shell even at low temperatures and that catalysts obtained from ligand-stabilized nanoparticles can be directly used as CO oxidation catalysts without any pretreatment.

Herein, we prove the usability of ligand-capped nanoparticles to steer SMSI effects for a Pt/Fe_3O_4 catalyst, for which, in contrast to other oxides, a SMSI effect was only recently reported and has received considerable attention since then.[18] The overgrowth of Pt by a FeO(111) monolayer was observed when Pt nanoparticles were deposited on Fe_3O_4(111) under UHV conditions.[19] In contrast to the studies mentioned above, such films were shown to result in superior CO oxidation activity also under oxidizing conditions.[20] These and other studies[21] suggest that highly active Pt catalysts can be obtained that are not limited to PROX.

For the preparation of Pt nanoparticles, we used the ethylene glycol (EG) method that has been described elsewhere[22] (see the Supporting Information) and is not just limited to the synthesis of Pt nanoparticles.[22,23] Since the ligand-free particles are modified with organic ligands in a subsequent step while the size and shape of the metal core is preserved, the approach allows the direct comparison of

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ligand-capped and -free particles on the same support, and thus the the role of the ligands in mediating metal–support interactions can be elucidated.

While one portion of the Pt nanoparticles was used directly to prepare a Pt/Fe_3O_4 catalyst by application of a colloidal deposition method, another portion of the particles was modified with dodecylamine (DDA) in a subsequent step and also deposited on nanocrystalline Fe_3O_4 (for details see the Supporting Information).

Whereas the colloidal solution of the ligand-free particles turned colorless instantaneously during the deposition, the solution of the DDA-capped particles remained black until solvent evaporation was complete, indicating that the interaction in the latter case is noticeably weaker because of the ligand shell.

As can be inferred from Figure 1 a,b, the size and shape of the particles are similar in both cases, namely 2.3 (±0.2) nm on average with quasi-spherical shape. However, a closer look at Figure 1 a reveals that a few of the ligand-free Pt particles seem to be encapsulated. Although a graphitic overlayer formed under the influence of the electron beam cannot be fully ruled out, this might point to an overgrowth by the iron oxide support in analogy to a similar result recently reported for a Pt/WO_3 catalysts for which similar shell structures were observed.[9] In contrast, such overlayers are not observed in Figure 1 b, probably because of protection by the ligands. According to TEM, the structural situation is unchanged also after catalytic measurements (Figure 1 c,d).

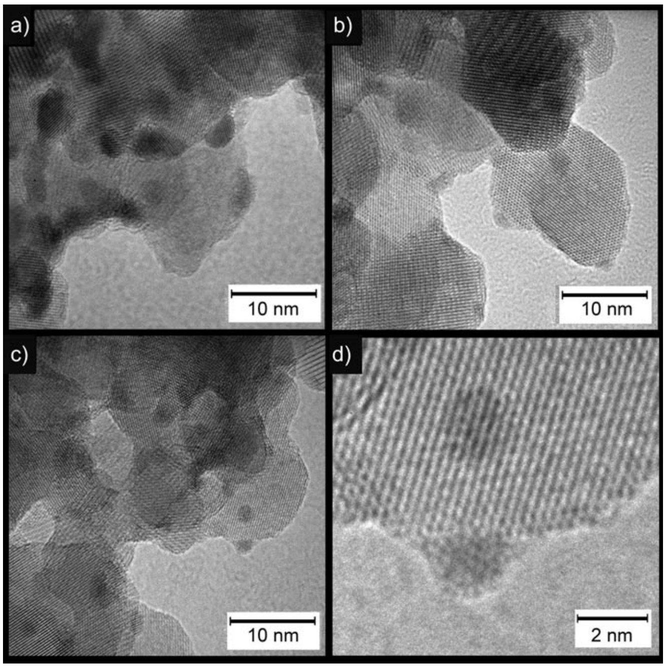

Figure 1. TEM images of a) ligand-free Pt on Fe_3O_4, b) DDA-capped Pt on Fe_3O_4 ("as prepared"), c) DDA-capped Pt on Fe_3O_4 after catalytic CO oxidation ("activated"), and d) larger magnification of the sample depicted in (c).

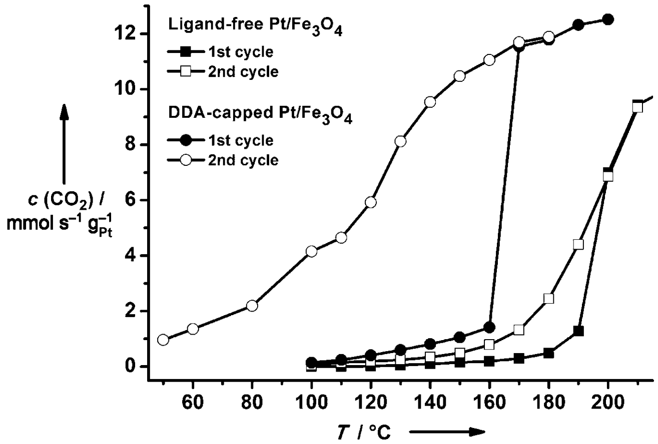

Figure 2. Catalytic activity for CO oxidation on Fe_3O_4-supported ligand-free and DDA-capped Pt. Reaction conditions: 3 vol% CO in synthetic air (total flow: 50 mL min^{-1}).

The ligand-free sample (Figure 2) shows a temperature dependence of the activity for CO oxidation that is comparable to that of Pt catalysts on irreducible supports such as γ-Al_2O_3.[17b] When the DDA-capped sample is heated up to 160 °C for the first time, its activity is initially similar to that of the ligand-free sample. At $T > 160$ °C, however, a sudden jump occurs leading to almost full conversion of CO. In repeated heating cycles, the DDA-capped sample exhibits high activity already at low temperatures ($T \approx 100$ °C); this activity can be maintained for several days also without addition of moisture which proved to be essential in other cases.[18c,24] Neither the pure Fe_3O_4 nor DDA-capped Pt nanoparticles synthesized by the same method but deposited on an inert support were found to have a comparable activity (see Figure S2). (Please note that such a highly active system could also be obtained for thiol-capped Pt/Fe_3O_4, see Figure S3.) This unexpected result suggests that the ligand capping can indeed act as a mediator to modify and tune a strong metal–support interaction.

The observed activation of the ligand-capped particles at 170 °C can be explained by the removal of ligands around this temperature. Similar activation was recently reported by Liu et al.[25] for colloidally prepared Au nanoparticles. Indeed, thermogravimetric measurements (see Figure S4) confirmed that in this temperature regime the first loss of DDA occurs.

To clarify the origin of the high catalytic activity of the ligand-capped sample, we carried out several experiments. First of all, in order to characterize the chemical state of the surface, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied, using CO as a probe molecule. The bottom spectrum in Figure 3 a shows that CO adsorption on ligand-free Pt results in two bands. Interestingly, the most pronounced band (2110 cm^{-1}) can be assigned to CO linearly adsorbed on oxidic Pt.[26] Apparently, the strong interaction between Pt and the Fe_3O_4 support leads to significant formation of oxidic Pt species.

The weaker band at 2072 cm^{-1} points to the linear adsorption of CO to metallic Pt[26] proving that small parts of the surface are actually not oxidized. If oxygen is additionally present (other spectra in Figure 3 a)), only the latter band disappears at temperatures above 180 °C accompanied by an increasing signal for CO_2 in the gas phase

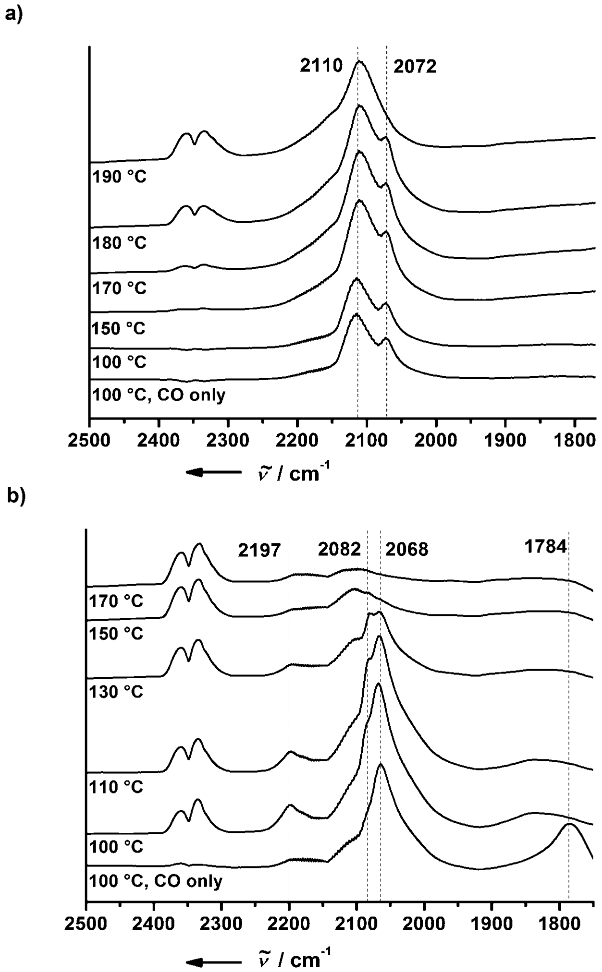

Figure 3. DRIFT spectra of pristine samples of a) ligand-free Pt on Fe_3O_4 and b) DDA-capped Pt on Fe_3O_4 under CO adsorption and CO oxidation conditions (for details see the Supporting Information).

($\approx$2350 cm^{-1}). Thus, in agreement with a Pt/Al_2O_3 catalyst,[27] the active species for the ligand-free sample is apparently CO linearly adsorbed on metallic Pt.

In the case of the pristine DDA-capped Pt (Figure 3b)) exposed to CO and O_2, the most dominant peak (2068 cm^{-1}) indicates that a large part of the Pt surface must be in the metallic state,[26] whereas the shoulder at 2082 cm^{-1} is characteristic for CO adsorption on $Pt^{\delta+}$ as could be expected in the vicinity of oxidized Pt.[28] (Please note that the band at 2197 cm^{-1} can be assigned to a nitrile species[29] and points to some ligand spillover of the amine from the Pt to the Fe_3O_4. The amine is then catalytically dehydrogenated by Fe_3O_4 to the corresponding nitrile.[30])

Interestingly, the spectrum of CO adsorption (bottom spectrum in Figure 3b) contains another peak at 1784 cm^{-1} which disappears already at temperatures as low as 100 °C in the presence of O_2 concomitantly with the appearance of a peak for gas-phase CO_2 and the onset of activity (see Figure 2), suggesting that it is associated with the active species at low temperatures. Recently, for a ceria-supported catalyst a band in this region was assigned to an interfacial Pt-CO-Ce^{3+} species.[31]

In an experiment without oxygen (exposure to pure CO), the intensity of this peak increased over time, while the signal for gas-phase CO_2 decreased (see Figure S5), indicating that even in the absence of O_2, small amounts of CO can be oxidized presumably by a Mars–van Krevelen-like mechanism[20] by means of oxygen from the support.

To check whether the dominant mechanism is indeed not Langmuir–Hinshelwood-like, measurements under CO-rich conditions were performed where CO poisoning usually prevents oxygen adsorption and thus CO oxidation. In contrast to the catalyst prepared from the ligand-free Pt, even in a tenfold excess of CO O_2 can be converted completely (see Figure S6). Here, the reaction takes place presumably at the border between metallic Pt, which provides CO adsorption sites, and FeO_x, which provides oxygen by a Mars–van Krevelen-type of mechanism.

To elucidate whether—as suggested by Sun et al.[20]—a thin FeO_x layer (not easily verifiable by TEM if it is composed of just a Fe-O or O-Fe-O layer as suggested by UHV studies[20]) on Pt is present supplying oxygen and causing the high catalytic activity, hydrogenation experiments using octadiene were performed. As this reaction is structure-insensitive, the activity should depend only on the number of active Pt sites. The activity decreased in the following order: “activated” ligand-capped > ligand-capped ≫ ligand-free (Figure S7). Briefly, the trend can be explained by the removal of ligands during activation and the lower hydrogenation activity of oxidized Pt compared to metallic Pt.[32] However, the activated sample was still significantly less active than identical DDA-capped Pt nanoparticles deposited on an inert support (Figure S8). This indicates a smaller number of active Pt sites because of partial FeO_x overgrowth compared to the sample on the inert support. Similar results were reported for classical SMSI systems.[11]

We conclude that by the use of protective organic capping agents, metal–support interactions can be tuned and optimized in order to increase the activity of supported metal catalysts. Whereas in the specific case studied here the deposition of ligand-free Pt particles results in a unfavorably strong interaction with the iron oxide support so that a large part of the Pt surface is oxidized and catalytically inactive, our results indicate that ligands, which are present during deposition but are removed under catalytic conditions, partly keep the particle surfaces metallic and partly allow for an overgrowth by a thin FeO_x overlayer. The reaction between CO on the Pt surface and oxygen delivered by the FeO_x overlayer at the border between the two phases can then bring about the observed high catalytic activity at low temperatures.

On account of the versatility of the synthetic approach, this route is by far not limited to the Pt/Fe_3O_4 system and may be applied to many metal/metal oxide combinations in future studies. Notably, a recent study of Liu et al.[25] indicates that a similar beneficial SMSI situation can be obtained for Au/FeO_x. On the one hand, this approach can be used to obtaina basic understanding of metal–support interactions contributing to the activity of a catalyst. On the other hand, highly active and maybe also selective catalysts can be created with this approach.

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