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Heterogeneous Catalysis

Ligand-Capped Pt Nanocrystals as Oxide-Supported Catalysts: FTIR Spectroscopic Investigations of the Adsorption and Oxidation of CO**

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Supported metals have a wide range of applications in heterogeneous catalysis; one of the key factors influencing the activity and selectivity is the particle size. The classical methods for preparing supported catalysts—impregnation and precipitation techniques—allow only poor control in this respect. A promising avenue for improvement is the use of metal nanoparticles prepared by means of colloidal chemistry, which allows particles to be obtained with well-defined size and shape through the use of stabilizing ligands.[1–4] However, it is not clear, to what extent catalytic activity can be obtained when the surface is partly covered by organic ligands.

In the present work we investigated this question for the example of Pt, which is used in the heterogeneous catalysis of, for example, hydrogenation reactions[5–8] and CO oxidation.[8,9] In studies of Pt nanoparticles synthesized with organic stabilizers, the organic shell was usually removed prior to catalysis.[5,8] Only a few catalytic studies exist in which ligands are present at the nanoparticle surface, even though the use of ligands can offer new possibilities for controlling activities and selectivities.[10,11] For example, high enantioselectivity was achieved in hydrogenation reactions in colloidal solution by using Pt nanoparticles stabilized with dihydrocinchonidine.[10] Furthermore, polymer-stabilized Pt and Pd nanoparticles were shown to be active for electron transfer and Suzuki cross-coupling reactions in colloidal solution.[12,13] In colloidal solution, it was also shown that CO can penetrate the ligand shell of Cu nanocrystals capped with hexadecylamine.[14] In a study of propene hydrogenation by relatively large (ca. 9 nm) polyacrylate-capped Pt nanoparticles supported on alumina, increased activity was observed when the polymer shell was removed by pretreatment.[6] For smaller supported Pt nanoparticles capped with nonpolymeric stabilizers, no catalytic investigations in the presence of organic ligands have been reported so far.

On this basis, the present work aimed to elucidate the potential of supported Pt nanoparticles capped with molecular ligands for catalysis. Thus, we prepared small Pt nanocrystals capped with dodecylamine (DDA) and hexanethiol (SC6), fixed them on alumina or silica, and studied their activity with respect to CO oxidation, which was selected as a test reaction. Catalytic activity could be observed in the presence of DDA and SC6, and the first studies of the influence of these ligands are presented herein.

TEM images of SC6- and DDA-capped Pt nanocrystals prepared by the method of Jana and Peng[1] are shown in Figure 1 a,d. The quasi-spherical particles have average sizes of 3.0 ± 1.0 and 2.7 ± 0.4 nm, respectively. By modifying the literature method,[1] we were also able to prepare DDA-capped Pt nanowires (Figure 1 g). The three types of Pt nanoparticles were deposited on oxide supports (SiO_2 or γ-Al_2O_3) with small catalyst loadings (<0.5 wt %). Figure 1 b,e,h shows TEM images of the supported catalysts obtained.

Figure 2 shows IR spectra of the samples after exposure to CO. A band appears at 2040–2050 cm^{-1} and can be assigned to linear CO adsorption on metallic Pt,[15] which demonstrates that small molecules such as CO can pass through the ligand shell and that parts of the metal surface are accessible for catalysis.

Whereas CO adsorption on single crystals of Pt usually results in a band at 2080–2100 cm^{-1},[16–18] the stretching frequency was found to decrease with decreasing particle size down to values below 2050 cm^{-1} for sizes of approximately 1 nm.[16,19] The stretching frequencies observed in our study are red-shifted by 20–25 cm^{-1} with respect to reference data[19,20] for the size regime around 3 nm (present work). Possible explanations include direct or indirect interactions with the organic stabilizer molecules. The presence of the ligands probably induces changes in the electronic structure at adjacent adsorption sites. The changes can then, in turn, influence the stretching frequency of adsorbed CO.

Figure 3 shows temperature-dependent IR spectra (a–c) of the samples upon exposure to a CO/O_2 mixture as well as an analysis of the gas phase (d–f). Relative to bands for the exposure to CO only, the bands for CO on Pt are blue-shifted after addition of oxygen, possibly owing to a coadsorption

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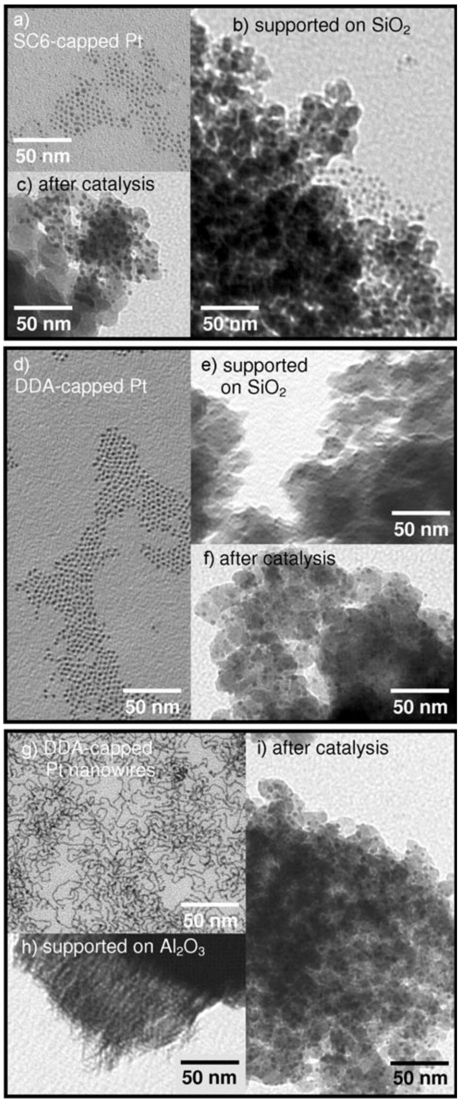

Figure 1. TEM images of the DDA- and SC6-capped Pt nanoparticles before (a,d,g) and after (b,e,h) deposition on oxide supports, as well as after the catalytic experiments (c,f,i).

effect. Furthermore, shifts observable upon heating point toward a different influence of the DDA and SC6 ligands.

In the case of the quasi-spherical, silica-supported particles, CO oxidation starts at 240–250 °C, as can be seen from the gas-phase analysis and the simultaneous disappearance of the IR band for adsorbed CO. (We note that the construction of the reaction cell precludes the determination of absolute conversion rates.) Evaluation of the C–H stretching region around 2900 cm^{-1} (see the Supporting Information for details) indicates that part of the ligands desorbed or decomposed above approximately 200 °C, whereas another part remained present on the surface even at 240–250 °C, where CO oxidation occurs. Moreover, as shown by TEM images acquired after the experiments (Figure 1 c,f), the morphology of the supported catalysts is conserved during CO oxidation at around 250 °C.

Heating of the DDA-capped, alumina-supported Pt nanowires in a CO/O_2 atmosphere at 160 °C leads to the

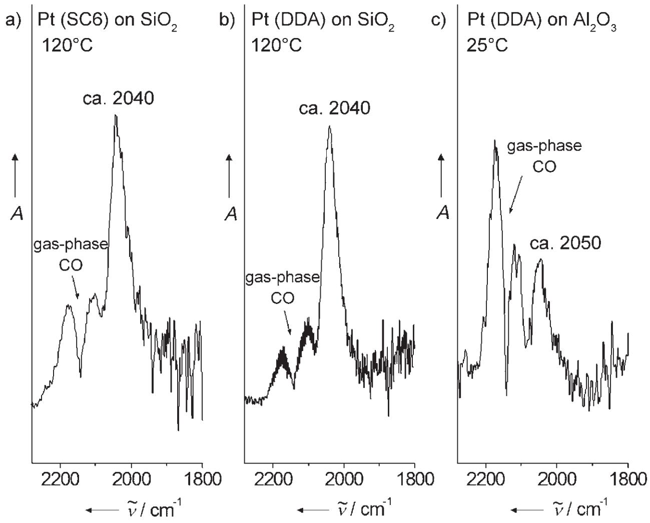

Figure 2. IR spectra of the samples after exposure to approximately 2.5 vol% CO in N_2 for a few minutes. The spectra were recorded after the CO supply was switched off (residual gas phase CO is still visible) and are referenced to background spectra recorded at 25 °C (c) and 120 °C (a,b) under a flow of pure N_2 prior to CO exposure.

appearance of a shoulder in the IR spectra at approximately 2077 cm^{-1} (D in Figure 3 c). TEM images before and after the catalytic experiments revealed a structural transition from nanowires to quasi-spherical particles (Figure 1 h,i). The shoulder in the IR spectra might be an indication that the structural transition occurred at around 160 °C in the CO/O_2 atmosphere. However, it is not possible to draw a definite conclusion in this respect, because a shoulder around 2080 cm^{-1} was also observed in other CO and CO/O_2 adsorption studies of quasi-spherical, supported Pt nanoparticles, and this feature was attributed to surface reconstruction.[19,21]

Activity for CO oxidation was observed already at around 180 °C for the last sample (Figure 3 c,f). Careful evaluation of the C–H stretching region (see the Supporting Information for details) indicated that the loss of ligands is much smaller than with the samples discussed above. This result is also in agreement with thermogravimetric analysis of octadecylamine-capped Pt nanoparticles which revealed that less than 15 % of the ligand shell was lost up to 200 °C, and around 40 % of the organic shell was lost at 250 °C.[22] The differences in activity in the studied cases might be due to the morphology, support effects, or differences in the degree of surface coverage by the ligand molecules. The structural transition from nanowires to quasi-spherical particles might play some role as well. Further studies are required to elucidate systematically the influence of the different parameters.

Finally, a few experiments were performed with the alumina-supported sample to check reversibility. After the temperature was lowered to 160 °C and the CO supply was switched off and then on again, a sharp band of adsorbed CO appeared at approximately 2089 cm^{-1}, and the CO oxidation reaction was stopped. Lévy et al. interpreted a similar band at 2085 cm^{-1} as CO linearly bound to partially oxidized platinum.[23] After the sample was again heated to around 190 °C,

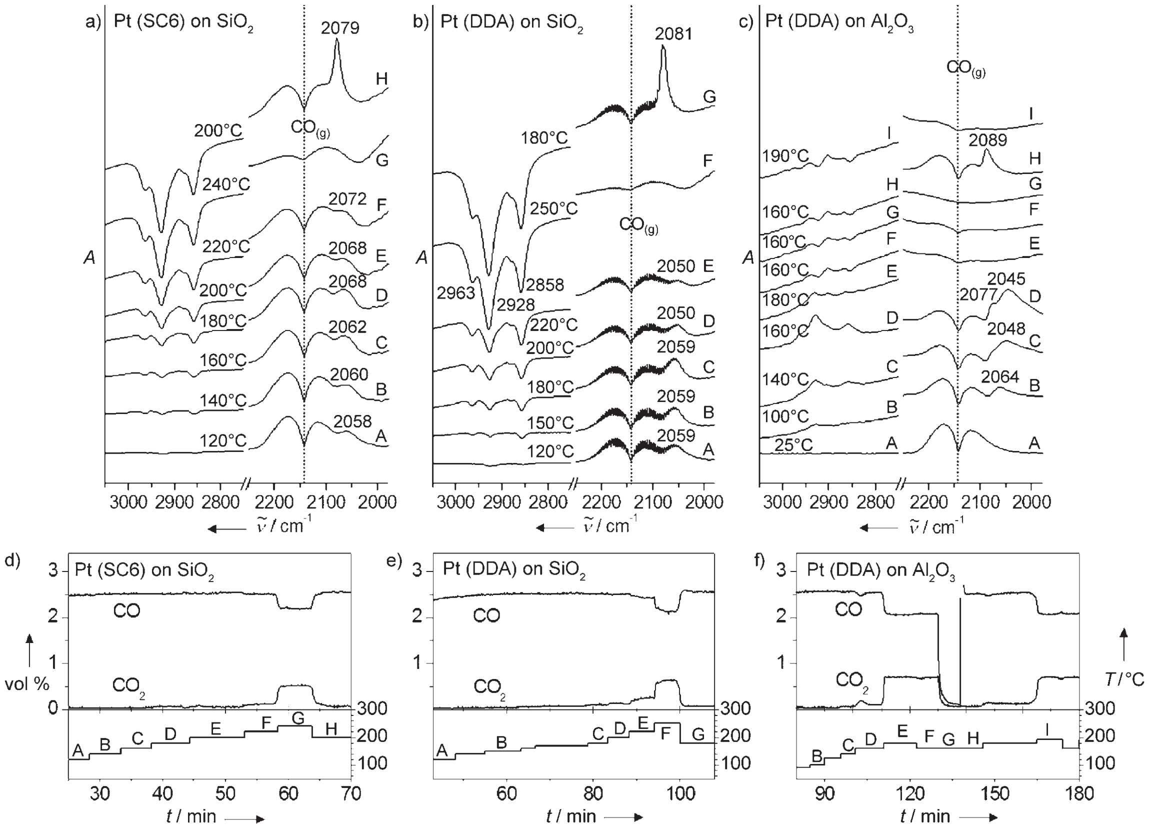

Figure 3. a–c) IR spectra of the ligand-capped, supported Pt nanoparticles upon exposure to ca. 2.5 vol% CO and ca. 2 vol% O_2 in N_2 (exception: G in (c): CO switched off). The spectra are referenced to background spectra recorded at 25 °C (c) and 120 °C (a,b) under a flow of pure N_2 prior to exposure to CO and O_2. d–f) Concentrations of CO and CO_2 and the applied temperatures as a function of time. The labels A–I assign the spectra in part (a–c) to the time points at which they were recorded.

the band disappeared and the initial activity for CO oxidation was restored (Figure 3).

In summary, our work demonstrates that colloidally prepared Pt nanoparticles capped with organic ligands appear to be suitable as supported catalysts. CO adsorption experiments have clearly shown that small molecules such as CO can pass through the ligand shell and adsorb on free areas of the Pt surface. Furthermore, activity for CO oxidation was observed in the presence of stabilizing molecules. The general applicability of the ligand-stabilized Pt nanoparticles as oxide-supported catalysts demonstrates that these systems have great potential as catalysts for more-complex reactions in which the ligand shell offers new perspectives to influence activity and selectivity.

Experimental Section

DDA-capped Pt nanocrystals were prepared from a $PtCl_4$ precursor according to a procedure developed by Jana and Peng.[1] SC6-capped particles were obtained by ligand exchange. Also by following established procedures,[1] the product of the synthesis with DDA was mixed prior to the postpreparative purification step with a solution of SC6 in toluene (1:1 molar ratio of SC6 to Pt) and stirred for around 15 min at room temperature. DDA-capped Pt nanowires were fabricated by performing the synthesis according to the literature method[1] but with absolute amounts of reactants 9 times higher. The colloidal solution obtained was then concentrated in a rotary evaporator for 1 h at 40 °C. This procedure yielded Pt nanowires with a thickness of about 2 nm.

IR spectroscopy was performed in diffuse-reflection geometry (DRIFTS) with an FTIR spectrometer (Biorad). Samples were pressed into pellets and studied in a reaction cell equipped with a gas-supply system, heating unit, and photometric detector (Hartmann & Braun URAS 10E) for CO/CO_2 analysis. The cell with the pellet inside was evacuated for a few minutes prior to measurement. Spectra were recorded with a resolution of 8 cm^{-1} under a continuous gas flow with N_2 as carrier gas.

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