Colloidally prepared platinum nanoparticles deposited on iron oxide studied by XAFS

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Abstract. Colloidal chemistry is an attractive method for the preparation of metal nanoparticles with well-defined shape and size rendering. This preparation technique is particularly interesting for the fabrication of heterogeneous catalysts, where size and shape play a key role for the catalytic properties. Nevertheless, the metal nanoparticles synthesized by colloidal approaches are often surrounded by a shell of organic ligands stabilizing the particles during the growth process. The influence of the ligands on the interaction with the support and the catalytic reaction was studied by x-ray absorption spectroscopy (XAS). It was found that the activity of the metallic Pt nanoparticles previously protected by organic ligands is higher in CO reaction than for unprotected nanoparticles deposited on iron oxide.

1. Introduction

The catalytic properties of the metal nanoparticles depend on their size, shape and – if present – on the nature of a surrounding ligand or polymer shell [1]. Heterogeneous catalysts in the form of supported nanoparticles are traditionally prepared by wet-impregnation or chemical precipitation methods. These methods often offer a limited control over the size of the noble metal catalyst which additionally depends on the nature of the supporting material. Generally, the nanoparticles are deposited on supports, such as metal oxides, zeolites or carbon. However, due to undesired metal-support interactions during deposition the support can change or diminish catalytic activity of the noble metal catalyst. Here, the use of preparation methods allowing to prepare uniform nanoparticles and to control the metal-support interactions is advantageous. This is the case for the colloidal synthesis of the metal catalysts [2]. However, a problem could arise from the fact that the prepared nanoparticles are often stabilized by organic ligands added during the synthesis. On the one hand they can e.g. stabilize the particles against aggregation and agglomeration [3]; on the other hand they could have detrimental effects on the catalytic activity in the case of heterogeneous gas-phase catalysis. Therefore, the usual approach is to remove the ligands prior to the catalytic reaction.

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On the contrary, our group and others have shown that the performance of an iron supported Pt catalyst can be enhanced with respect to CO-oxidation by the use of such organic stabilizers [2, 4]. The enhanced effect can be attributed to the ligand-induced blocking of a first, strong chemical interaction that occurs during the deposition of the colloidal platinum nanoparticles onto the iron oxide support. In order to achieve comprehensive knowledge about this class of materials, X-ray absorption spectroscopy (XAS) was applied. Specifically, a ligand stabilized platinum iron oxide catalyst prepared by a one pot method in diethylene glycol was studied.

2. Experimental

For the preparation of the catalyst, first nanocrystalline iron oxide was prepared by the so-called polyol method in diethylene glycol, i.e., the decomposition of iron acetylacetonate at 200°C for 2 hours [5]. After a cool down period, platinum acetylacetonate was added to the solution and stirred for 30 minutes. For the formation of the platinum nanoparticles in the presence of iron oxide, the solution was heated up for 2 hours at 180°C again. At the end of the synthesis, the catalyst was precipitated by acetone and dried under air. Under these conditions, residual diethylene glycol (DEG) will stay adsorbed on the surface of the particles thus acting as ligands. These ligand-capped Pt nanoparticles will be called P1 in the following. After using them for CO oxidation (called activated as the ligands desorb during the process, as discussed in the following), the particles, called P2, were studied by x-ray absorption spectroscopy (XAS). The x-ray absorption fine structure (XAFS) measurements were performed at beamline C at the Hasylab, DESY in Hamburg, Germany. The beam was monochromatized by a Si(311) monochromator. The samples were pressed into pellets and fixed onto the sample holder. The XAFS spectra were recorded in fluorescence mode using the 7 cell SDD detector.

XAFS spectra were processed according standard steps by applying Athena software; the structural parameters were obtained using the program Artemis [6]. The scattering paths Pt-Pt and Pt-Fe for metal Pt used for fitting of the EXAFS data were generated by the FEFF6 code [7]. The EXAFS oscillation in the k range 4–11 Å⁻¹ were Fourier transformed (FT’s), using a Kaiser- Bessel window. The fitting of one coordination shell was performed in R space in the range 1.3– 3.3 Å.

The size of the metal Pt nanoparticles was determined by transmission electron microscopy (TEM) for sample P1 and P2, respectively. For the CO oxidation experiments, a suitable laboratory reactor (fixed-bed type reactor with a heating system) was used. Precautions were taken to avoid mass-transport limitations and electrostatic charging. The powder catalysts were pressed and sieved into 0.31-0.45 mm grains, from which 10 mg were then mixed with quartz (800 mg, diameter 0.4-0.8 mm, Roth, calcinated at 1000 °C for 6 h) and placed between quartz wool into the reactor. The measurements were performed under continuous flow conditions with 3 vol.-% CO in synthetic air (total flow: 50 mL/min) unless otherwise noted. The components in the product stream were analysed with a photometric detector for CO/CO2 (URAS 3G, Hartmann & Braun).

3. Results and Discussion

The XANES spectra collected at the L₃ edge for metal Pt nanoparticles supported on Fe₂O₃ and Pt foil are depicted in Figure 1. The spectra acquired for the nanoparticles show features characteristic for metallic Pt. A double peak structure at the 11.578 keV and 11.590 keV after the white line are present in both studied samples. The intensity of the white line of the sample P2 is higher than for metallic Pt and sample P1, indicating the existence some oxidized Pt.

On the contrary, the EXAFS data for sample P2 could be well fitted assuming the presence of only metallic Pt. The determined Pt-Pt bond lengths are shorter by about 0.03 Å as compared to bulk Pt, 2.74 Å and 2.77 Å respectively, Table 1. The best fit for sample P1 was obtained assuming the presence Pt-Pt and Pt-Fe distances in the model. The small inclusion of Fe was found to be in the range of ~ 8% and could be the result of an interaction with the support. The Pt-Pt distance was found to be 2.72 Å in comparison to 2.77 Å for bulk Pt. The Pt-Fe bond lengths were also shorter than for bulk fcc PtFe, namely 2.68 Å as compared to 2.72 Å for bulk FePt. The coordination numbers 12
found for both samples are in agreement with coordination number for metallic Pt nanoparticles and compatible with an average nanoparticles size of 5 nm [8]. The shorter Pt-Pt distances observed for sample P1 in comparison to bulk Pt could be the result of the particle size. The adsorption of residual carbon monoxide on the sample P2 after catalysis might result in bond relaxation thereby expanding the particles [9].

Figure 1. Pt L3 edge XANES spectra for Pt/Fe3O4 ligand-capped (DEG) (thin line) (P1) and activated (circle) (P2) in comparison with reference Pt foil.

Table 4. The numerical results of the fitting EXAFS oscillation recorded for investigated Pt/Fe3O4 ligand-capped (P1) and activated (P2), respectively.

| Pair    | R (Å)   | σ² (Å²) | N  |
|---------|---------|---------|----|
| P1      | Pt-Pt   | 2.72(2) | 0.010 | 11  |
|         | Pt-Fe   | 2.68(1) | 0.003 | 1   |
| P2      | Pt-Pt   | 2.74(1) | 0.009 | 12  |
| Pt foil | Pt-Pt   | 2.77(2) | 0.005 | 12  |

In order to study the influence of organic ligands on the catalytic properties, CO oxidation was performed for all catalysts. Figure 2 shows the catalytic performance of unprotected 2 nm Pt nanoparticles (preparation: see ref. [2]), 2 nm particles protected with dodecylamine (DDA) (another type of ligand: for details see ref. 2) and the new DEG covered platinum particles 3 and 5 nm size described in this paper. The activity of the unprotected Pt nanoparticles is comparable to the activity of nanoparticles on irreducible supports, such as γ-Al2O3 [10]. On the other hand, if DDA capped platinum nanoparticles are deposited on the iron oxide support, the catalysts shows high catalytic activity after desorption/decomposition of the ligands above 160°C. If the catalytic reaction is repeated in a second cycle, activity is also observed below 160°C. Even at 100°C, appreciable conversion rates are detected. A comparable situation, however, with even higher activities in the second cycle of the catalytic CO-oxidation, can be reached by the use of the DEG covered platinum-iron oxide catalysts. After the activation of the catalyst in the first cycle at a temperature of 170°C - which can be assigned to desorption/decomposition temperature of DEG -, the catalysts show a 20% higher conversion rate in the low temperature region (<160°C), compared to the DDA-capped platinum nanoparticles on iron oxide. As concluded from the infrared spectra acquired for the DEG covered particles, the adsorption
of linear CO on platinum (not shown here) lead to a band at 2044 cm\(^{-1}\), which indicates metallic state at the surface of the platinum nanoparticles. However, by applying reaction conditions, a shift of this band to lower wavelength (2035 cm\(^{-1}\)) was observed which might be attributable to an incorporation of iron atoms into the platinum lattice [11].

The XANES data after catalysis show a small indication of oxidized Pt, while the EXAFS data show no differences to the situation before catalysis (metallic Pt for sample P2). This behaviour is in marked contrast to smaller unprotected and DDA capped particles. As detailed in ref. 2, they get largely (unprotected) or partially (ligand-capped) oxidized. Nevertheless, the small (3 nm) and large (5 nm) particles show the same behaviour under catalytic conditions. As was concluded for the small particles, an SMSI effect with the iron oxide, coming into action after desorption of the ligands in the first catalytic run, gives rise for the remarkable low temperature catalytic activity in the second and following runs. This SMSI effect can – independent of the particle size – only be achieved by using a ligand assisted deposition technique. Further experiments are under way to elucidate the exact mechanism.

4. Conclusion
The XAFS data prove that Pt nanoparticles colloidally prepared by an one pot method in DEG and in the presence of iron oxide, have a strong metallic character. The DEG solvent and simultaneously ligand solution protect the formed metal Pt nanoparticles as well as the iron oxide nanoparticles against a strong primer interaction, previously observed for smaller particles. Nevertheless, the ligands can be removed by activation at temperatures of 170°C. In the following the particles are active for CO oxidation at temperatures significantly lower than observed for conventional Pt catalysts. This activity can be ascribed to an SMSI effect between Pt and the iron oxide being only effective if the particles are protected by the ligands while being deposited or created in the presence on the support.

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