A combined in situ EXAFS / on-line FT-IR study: Unequivocal identification of the active species in Pd-catalysed liquid-phase alcohol oxidation

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Aerobic alcohol oxidation over Pd- and Pt-based catalysts is an important process in fine chemistry and has attracted considerable attention during the past decades [1]. However, the mechanism is still a matter of ongoing debate and an unambiguous proof of the nature of the active noble metal sites appears of fundamental importance [1-3]. In previous studies, also applying in situ X-ray absorption spectroscopy, we found that metallic palladium or platinum are the active species and thus the dehydrogenation step is prevalent [2]. Nevertheless, it has been speculated from other in situ XAS measurements that the catalytic activity was higher on oxidized noble metal particles than after their reduction by the reactant alcohol [3]. However, the spectroscopic studies were not performed “truly” in situ, as required for the determination of structure-performance relationships [4]. For such investigations the catalyst should be ideally present as powder or shell impregnated particles and the catalytic activity should be simultaneously measured on-line [5].

This prompted us to design a setup that allows monitoring the structural changes in liquid organic media by XAS and the catalytic activity by on-line FT-IR spectroscopy. It consists of a spectroscopic reaction cell in which the catalyst is placed (as powder and/or shell-impregnated catalyst). The cell mimics the conditions of a continuous-flow fixed-bed reactor and is equipped with X-ray transparent windows for the spectroscopic studies. A liquid pump allows feeding the liquid reactants into the in situ reaction cell, which can be heated by a specially designed oven. Monitoring of reaction progress was achieved by a transmission flow-through IR cell, which was connected to the outlet of the in situ reaction cell. The experiments were performed at beamline X1 at HASYLAB (DESY, Hamburg). Both a commercial 5%Pd/Al₂O₃ catalyst in the form of a powder (ca. 50 µm mean particle size) and a commercial 0.5%Pd/Al₂O₃ catalyst in the form of pellets (shell impregnated, sieved fraction of the crushed catalyst 200 µm < d < 300 µm, active catalytic layer of ca. 60 µm, as determined by SEM) were used for the studies. The spectra were analysed using the Athena 0.8.049 software [6] and the EXAFS spectra were fitted using the FEFF 6.0 code [7].

The catalytic activity and the catalyst structure were investigated during the aerobic oxidation of benzyl alcohol before and after reduction of the catalyst in hydrogen, applying in both cases the same reaction conditions. The reaction temperature was set at 50°C, where the alcohol alone was not expected to reduce palladium oxide but the catalytic activity was high enough to be monitored by on-line FT-IR.

Figure 1 shows the results from the combined study using in situ X-ray absorption spectroscopy and on-line product analysis by FTIR for the 5%Pd/Al₂O₃ catalyst. While heating the as-prepared catalyst to the reaction temperature of 50°C in cyclohexane and exposing it to the reaction mixture of benzyl alcohol/oxygen/cyclohexane (200 µl benzyl alcohol in 100 ml cyclohexane, saturated with oxygen, steps a and b), the structure of the catalyst remained in the same partially oxidized state. Hardly any catalytic activity was measured under these conditions (Fig. 1, FT-IR window) as also supported by corresponding laboratory experiments (not shown). No change in the region 1700 – 1720 cm⁻¹ (carbonyl stretching region) was observed and the C-O stretching vibration at 1018 cm⁻¹ was constant and clearly visible. During exposure to hydrogen saturated cyclohexane, the catalyst was completely reduced after about 30 min, as derived from both the XANES (Fig. 1, XANES window, step c) and EXAFS data (Fig. 1, EXAFS window, step c). From the EXAFS analysis it further emerged that palladium hydride is formed (backscattering from nearest neighbor Pd-atoms decreases and the Pd-Pd-distance increases). This leads both to a more elongated EXAFS function and a shift in the Fourier transformed EXAFS spectra to higher R-values (Fig. 1, EXAFS window). Upon exposure of the reduced catalyst to the reaction mixture consisting of benzyl alcohol/oxygen/cyclohexane at 50°C, a much higher catalytic activity was achieved, as indicated by the on-line FT-IR measurements (Fig. 1, FT-IR window, step d). In the XANES spectra hardly any change was observed indicating that palladium remained metallic during the aerobic oxidation of the alcohol (Fig. 1, XANES widow, step d). The EXAFS data showed that the hydride was immediately decomposed again, but no oxidation of the Pd particles was observed. The on-line FT-IR measurements showed a certain deactivation of the catalyst with time-on-stream which may be due to accumulation of some by-products on
the catalyst surface. However, also after longer time-on-stream the structure of the catalyst remained in the same state (cf. EXAFS) and the catalytic activity was strikingly higher (> 50 times) than that observed when using the oxidized palladium catalyst.

In summary, our results demonstrate that palladium oxide exhibits hardly any catalytic activity for alcohol oxidation at 50 °C, while metallic Pd particles are much more active. This is in agreement with the dehydrogenation mechanism and further details can be found in reference [7]. In addition, we were able to observe the catalytic activity on-line by FT-IR, while simultaneously probing the structure of the catalyst by X-ray absorption spectroscopy. The presented approach can be regarded as an important step forward to generally derive structure-activity relationships under dynamic reaction conditions also in liquid-phase reactions, which up to now have been much less studied than gas phase reactions, where EXAFS is typically combined with on-line mass spectrometry [8].

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References