

# In situ EXAFS study of Pd/Al<sub>2</sub>O<sub>3</sub> during aerobic oxidation of cinnamyl alcohol in an organic solvent

Jan-Dierk Grunwaldt,\* Csilla Keresszegi, Tamas Mallat, and Alfons Baiker

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH Hönggerberg HCI, CH-8093 Zurich, Switzerland

Received 17 July 2002; revised 14 August 2002; accepted 20 September 2002

## Abstract

Dynamic structural changes of an alumina-supported palladium catalyst were followed by in situ EXAFS and quick EXAFS (QEXAFS) during oxidative dehydrogenation of cinnamyl alcohol. QEXAFS studies in a continuous flow fixed-bed reactor revealed that the palladium constituent was reduced within 1 h during exposure of the catalyst to a toluenic cinnamyl alcohol flow in Ar. After saturation of the feed with 5% O<sub>2</sub>/He the product distribution was similar to that observed in a slurry reactor and indicated dehydrogenation, hydrogenation, hydrogenolysis, and decarbonylation reactions, catalyzed by metallic Pd. The studies show that dynamic structural changes and the catalytic performance of an industrial supported metal catalyst in an organic solvent can be monitored simultaneously.

© 2002 Elsevier Science (USA). All rights reserved.

**Keywords:** EXAFS; QEXAFS; In situ spectroscopy; Pd/Al<sub>2</sub>O<sub>3</sub>; Oxidation; Cinnamyl alcohol; Dehydrogenation; Decarbonylation

## 1. Introduction

Selective aerobic oxidation of alcohols to carbonyl compounds over supported noble metal catalysts is a practically important and environmentally friendly process, which has been thoroughly investigated in the past decades (for reviews see [1–4]). The reactions are commonly carried out under mild conditions in water or in an apolar organic solvent. The latter is favored for the synthesis of activated carbonyl compounds in order to minimize their hydration and rapid further oxidation to carboxylic acids.

Critical and still debated questions are the oxidation state of the active sites during alcohol oxidation and the role of oxygen in the reaction mechanism and in catalyst deactivation. According to the various models proposed [1–4], the role of oxygen may be simply the oxidation of the co-product hydrogen, it may accelerate the reaction by oxidation of strongly adsorbed impurities (alcohol degradation products), or it may be directly involved in hydrogen abstraction from the adsorbed alcohol (alkoxy) species.

Answering the above questions necessitates in situ studies. The oxidation state of the metal during reaction can be followed by measuring the catalyst potential ([5,6] and ref-

erences therein). The technique is highly surface sensitive but requires a conductive medium, and surface impurities may complicate interpretation of the results. Very recently, ATR-IR spectroscopy has been found to be effective for monitoring the adsorbed surface species on Pt metals in solutions [7,8].

Dutch groups [9,10] applied EXAFS to the characterization of Pt-based catalysts in an aqueous solution. Also other groups reported on in situ EXAFS cells for studying the liquid/solid interface of heterogeneous catalysts (e.g., [11]). In situ catalyst characterization by EXAFS during gas/solid type reactions has been widely reported (e.g., [12–14] and references therein). A further challenge is the investigation of dynamic changes. For gas/solid-type reactions both quick EXAFS (QEXAFS) and dispersive EXAFS (DEXAFS) have been used for this purpose [13–16], but to our knowledge they have not been reported for liquid/solid-type reactions. QEXAFS has the inherent advantage that it is less sensitive to the heterogeneity usually encountered in solid catalysts, and thus we decided to use this method to monitor the catalyst structure in liquid organic phase.

Here we report on dynamic structural changes of a 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst observed by QEXAFS during aerobic oxidation of cinnamyl alcohol in toluene. A continuous-flow fixed-bed reactor has been developed that allowed catalytic and EXAFS measurements in a closed system, so

\* Corresponding author.

E-mail address: [grunwaldt@tech.chem.ethz.ch](mailto:grunwaldt@tech.chem.ethz.ch) (J.-D. Grunwaldt).

the reactor is also applicable to reactions in organic solvents. The catalytic results are compared to those obtained in a conventional laboratory slurry reactor.

## 2. Experimental

### 2.1. Materials

A 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> (Johnson Matthey 324, mean particle size 3.4 nm, as determined by TEM) and toluene (J.T. Baker, > 99.5%) were used as received. *trans*-Cinnamyl alcohol (Acros, 98%) was purified by recrystallization from petroleum ether (99.3%).

### 2.2. Alcohol dehydrogenation in the EXAFS reactor cell

Working with organic solvents and gases at synchrotrons requires special security handling. Here we used a closed system with all gas-out lines connected to the exhaust system. Appropriate ventilation and gas sensors are also recommended. The principal setup is shown in Fig. 1. The reaction mixture (1 g cinnamyl alcohol in 100 ml toluene) and pure toluene were stored in two glass tanks, which allowed deoxygenation with Ar or saturation with oxygen

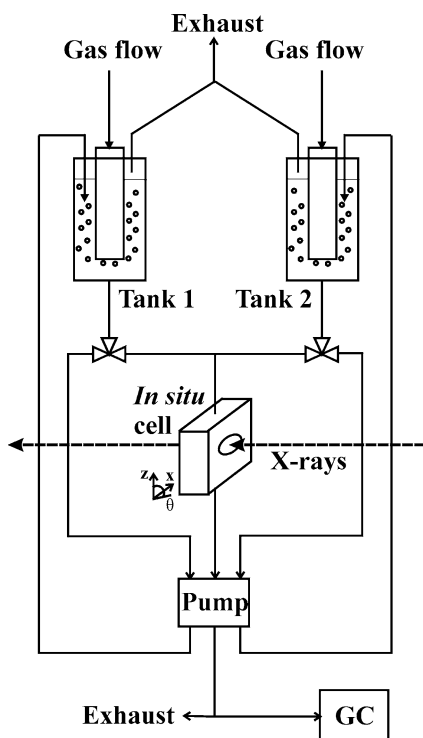


Fig. 1. Schematic presentation of the experimental setup for the in situ EXAFS measurements. The liquid is stored in two glass tanks and saturated with appropriate gas mixtures. The liquid is pumped through the in situ cell, which is aligned in the beam by an  $x, z, \theta$ -table. Product analysis can be performed by GC or other sampling techniques. All vessels are connected to the exhaust system to prevent solvent/gas exposure of the surroundings (cf. description in the Experimental part).

(5% O<sub>2</sub> in He). The liquids could be transferred by a pump (ISMATEC, REGLO 100) through the tubing back to the tank or to the reaction cell and then to exhaust (collector vessel). All vessels contained a line to the gas exhaust system to prevent any gas or solvent exposure of the surroundings. The liquid feed flow rate was 0.13 ml min<sup>-1</sup>. The reactor cell (ca. 0.3 ml), containing a catalyst tablet of ca. 300 mg catalyst ( $d = 1.3$  cm), was thermostated at 55 °C. The reactor was fixed on an  $x, z, \theta$ -table to allow positioning of the cell in the beam. The X-rays passed through the reactor cell via X-ray transmittant windows (Al foil, Kapton).

At first deoxygenated toluene was fed to the catalyst; then the feed was changed to the deoxygenated toluenic solution of cinnamyl alcohol, and finally to the toluenic solution of cinnamyl alcohol saturated with 5% O<sub>2</sub> in He. Samples for GC analysis (Thermo Quest Trace 2000, equipped with an HP-FFAP capillary column and an FID detector) were taken from the collector vessel. Products were identified by GC-MS and by GC analysis of the corresponding authentic samples.

### 2.3. Alcohol dehydrogenation in a slurry reactor

Oxidation of cinnamyl alcohol was carried out in a flat-bottomed, magnetically stirred (750 min<sup>-1</sup>) glass reactor. At first, 0.10 g 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> (pre-reduced by hydrogen and reoxidized in air at 40 °C), 1.0 g alcohol, and 30 ml toluene were stirred at 65 °C in Ar for 90 min; then Ar was replaced by air (20 ml min<sup>-1</sup>) for 25 min. More details can be found elsewhere [8].

### 2.4. EXAFS analysis

The experiments were performed at the Hamburger Synchrotronlabor (HASYLAB at DESY, Germany) at beamline X1 using a Si (311) double-crystal monochromator. Higher harmonics were minimized by slightly detuning the crystals. Three ionization chambers filled with Ar were used to record the intensity of the incident and the transmitted X-rays (reactor cell located between the first and second ionization chambers, Ag reference foil for energy calibration between the second and third ionization chambers). Under stationary conditions EXAFS spectra were taken around the Pd *K*-edge in the step-scanning mode between 24,000 and 25,800 eV. Additionally, faster QEXAFS scans in the continuous scanning mode were recorded between 24,300 and 24,800 eV (3.5 min/scan). The raw data were energy-calibrated (Ag *K*-edge energy of the Ag-foil: 25,514 eV, first inflection point), background-corrected, and normalized using the WINXAS 2.1 software [17]. For QEXAFS data, Fourier transformation was applied to the  $k^3$ -weighted functions in the interval  $k = 2.8\text{--}10.5 \text{ \AA}^{-1}$ , and for EXAFS data in the interval  $k = 3.5\text{--}15.5 \text{ \AA}^{-1}$ .

### 3. Results and discussion

#### 3.1. Catalyst reduction during dehydrogenation of cinnamyl alcohol

Figure 2 gives an overview of the in situ QEXAFS data obtained on Pd/Al<sub>2</sub>O<sub>3</sub>, starting under oxygen-free conditions in toluene and changing to the toluenic cinnamyl alcohol solution (zero time). The catalyst, previously stored in air, is partially oxidized. No significant changes were observed when it was exposed to toluene, but a continuous transformation was detected during exposure to the toluenic cinnamyl alcohol solution. The strong whiteline in the starting spectra confirms that Pd was in an oxidized state before it contacted the alcohol reactant, and the metal oxide was successively reduced by cinnamyl alcohol. Simultaneously, dehydrogenation of cinnamyl alcohol was corroborated by GC analysis of the effluent. Only a few % conversion of cinnamyl alcohol was detected and the main product was cinnamaldehyde (over 90% selectivity). On this

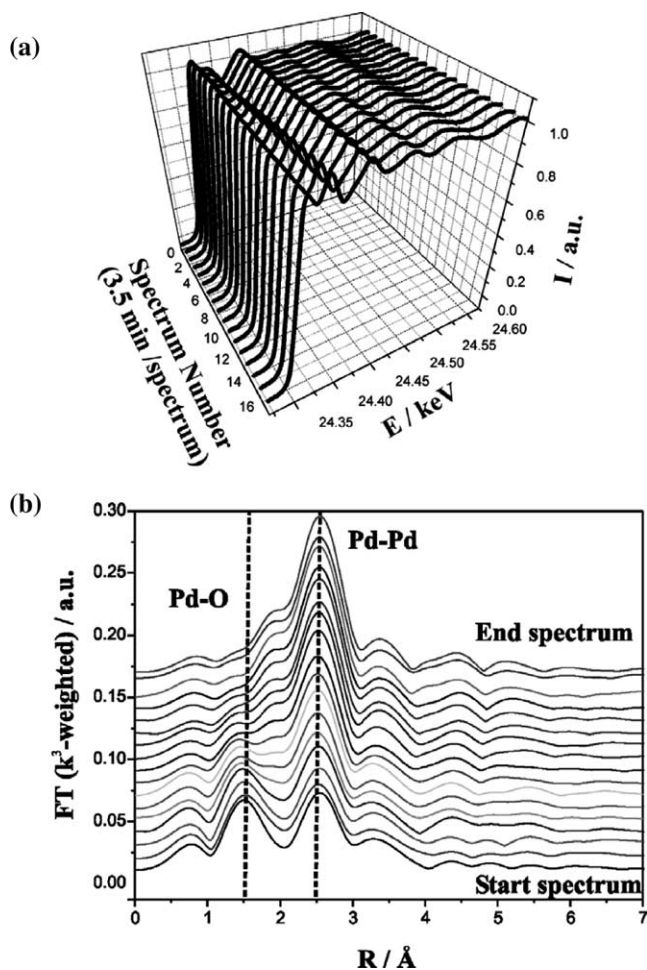


Fig. 2. QEXAFS spectra taken around the Pd *K*-edge in Ar atmosphere after the feed was changed from toluene to cinnamyl alcohol in toluene: (a) raw QEXAFS data—the time lag between the spectra is 3.5 min; (b) Fourier transformed QEXAFS spectra—dotted lines are given as a guide for the eye for the position of Pd–O and Pd–Pd scattering.

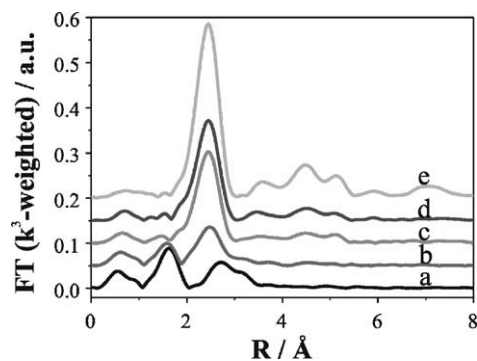


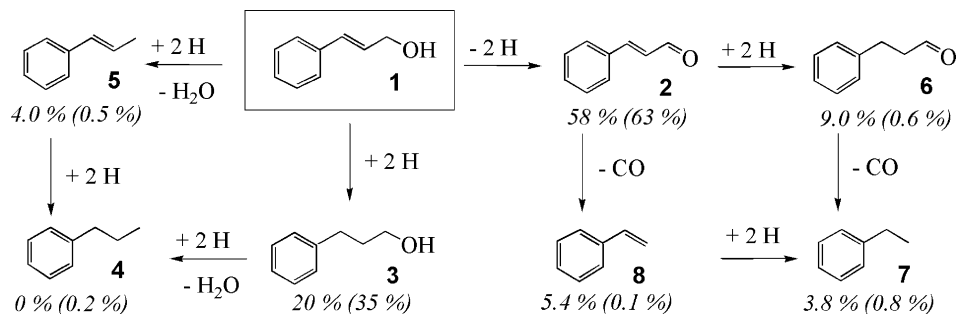
Fig. 3. Fourier transformed EXAFS spectra at the Pd *K*-edge of (a) PdO; (b) Pd/Al<sub>2</sub>O<sub>3</sub> “as received”; (c) 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> after reduction by the cinnamyl alcohol/toluene solution in Ar; (d) 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> after 120 min exposure to the cinnamyl alcohol/toluene solution saturated with 5% O<sub>2</sub> in He; (e) Pd foil.

partially oxidized catalyst the only detectable byproduct was 3-phenyl-1-propanol. This side reaction is typical for allylic alcohols and may be considered a transfer dehydrogenation reaction in which the reactant plays the role of hydrogen acceptor [18]. Parallel to reduction of Pd the product distribution changed dramatically, as will be shown below.

Since the QEXAFS data are of sufficient quality, Fourier transformation can be performed as well, as shown in Fig. 2b. While the starting spectrum in Fig. 2b shows both Pd–O and Pd–Pd contributions in the FT spectra, nearly no Pd–O contribution can be found after a time-on-stream of ca. 1 h. Figure 3c compares the Fourier transformed spectrum after 1 h on stream in Ar with model substances (Figs. 3a and 3e). The spectrum in Fig. 3c is similar to that of a Pd foil. The lower Pd–Pd scattering observed for the catalyst under reaction conditions is traced back to a coordination number smaller than that for the Pd-foil. Pd–O backscattering is not observed as in a PdO model sample or in the partially oxidized Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 3b: both Pd–O and Pd–Pd scattering peaks are present). This is supported by fitting the first Pd–O and Pd–Pd shell with phase and amplitude functions of Pd metal and PdO references. Only a Pd–Pd contribution with coordination number CN<sub>Pd–Pd</sub> = 10.0 and distance  $R_{\text{Pd–Pd}} = 0.276$  nm is found. This indicates a high degree of reduction of the catalyst by the alcohol, which is in agreement with conclusions from former EXAFS studies in an aqueous solution [9,10] and from catalyst potential measurements during cinnamyl alcohol oxidation on Pt-based catalysts [19].

#### 3.2. Oxidation state of Pd during oxidative dehydrogenation of cinnamyl alcohol

In the next step the toluenic cinnamyl alcohol solution saturated with 5% O<sub>2</sub> in He was fed into the reactor for an additional 120 min. The product distribution measured at the end of this period is shown in Scheme 1. Besides the target reaction, the transformation of cinnamyl alcohol (1) to cinnamaldehyde (2), several other products were



Scheme 1. Reaction network for the transformation of *trans*-cinnamyl alcohol over 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub>. The conversion after 2 h time-on-stream in the presence of 5% O<sub>2</sub>/He in the EXAFS reactor cell was 6.9%, as compared to the 99.8% achieved in a slurry reactor in air [8]. Selectivities are indicated below the formulas, together with the selectivities (in brackets) obtained in the slurry reactor. For conditions see the Experimental part.

produced by hydrogenation (**3**, **6**), hydrogenolysis (**5**), and decarbonylation (**7**, **8**) side reactions. The product distribution is compared to that obtained in a slurry reactor over the same catalyst in air [8]. Despite the strikingly different conversions and reaction conditions, there is a reasonably good qualitative agreement in the product composition. The only exception is that propylbenzene (**4**) did not form in the continuous EXAFS reactor cell. Another difference is the remarkably higher reaction rate observed in the slurry reactor, which is mainly attributed to the efficient mixing and the higher oxygen concentration (21% vs 5% in the EXAFS reactor cell). Another interesting point is that steady state was not completely reached in the EXAFS reactor cell after 2 h, as indicated by changes in the product composition. This may be an indication of some mass transport limitation in the fixed bed reactor. Nevertheless, the similar product distributions in the two reactors suggest that the results obtained in the EXAFS reactor cell are representative for the aerobic oxidation of cinnamyl alcohol over palladium. Due to the high alcohol/oxygen ratio in the feed and the high amount of catalyst, the catalyst remained in a reduced state, as also shown by the EXAFS spectrum in Fig. 3d and reflected by the fitting results: CN<sub>Pd–Pd</sub> = 9.7 and  $R_{\text{Pd–Pd}} = 0.276$  nm.

According to the “classical” dehydrogenation mechanism for this reaction [8,19], the noble metal catalyzes the hydrogen abstraction from the adsorbed reactant and in a subsequent step surface hydrogen is oxidized by adsorbed oxygen [1,4]. Formation of products **3** and **5–7** (Scheme 1) suggests that there was sufficient hydrogen available on the metal surface to allow hydrogenation and hydrogenolysis side reactions, even when oxygen was present in the feed.

Generalization of the results necessitates the extension of investigations to other reactants and catalysts, and also variation of the actual oxygen concentration on the catalyst surface. It will also be attempted to improve the reactor setup in order to minimize the dead volume and the amount of catalyst and to enhance the mass transfer in the EXAFS reactor cell.

## 4. Conclusion

The preliminary results of cinnamyl alcohol oxidation in a continuous flow fixed-bed reactor demonstrate, in accordance with previously reported studies, that in situ EXAFS studies in organic solvents are feasible. In analogy to studies of gaseous reactions, dynamic changes of the catalyst structure can be monitored by QEXAFS. These measurements give insight into the structure and bulk oxidation state of the catalyst during reaction. By applying supported metal catalysts that possess small metal particles, useful information on the liquid/solid interface can be obtained as well. The product compositions in the continuous flow fixed-bed reactor and in a slurry reactor were similar, though the reaction rate was remarkably lower in the continuous reactor. The main obstacle is to overcome possible diffusion limitations and an improved flow reactor cell is presently under construction. Nevertheless, the approach may improve our understanding of the mechanism of heterogeneously catalyzed reactions in organic liquid media.

## Acknowledgments

The authors thank the synchrotron facility HASYLAB in Hamburg, Germany, for providing beamtime for this work. The beamline staff at beamline X1, in particular N. Haack, E. Welter, and M. Hermann, as well as S. Hannemann and M. Ramin, are gratefully acknowledged for their support during the measurements. P. Trüssel (LTC, mechanical workshop) and M. Wohlwend (LTC, electronic workshop) are kindly acknowledged for their valuable support in the design of the in situ setup and we thank T. Bürgi for fruitful discussions.

## References

- [1] P. Vinke, D. de Wit, A.T.J.W. Goede, H. van Bekkum, *Stud. Surf. Sci. Catal.* 72 (1992) 1.
- [2] T. Mallat, A. Baiker, *Catal. Today* 19 (1994) 247.
- [3] J.H.J. Kluytmans, A.P. Markusse, B.F.M. Kuster, G.B. Marin, J.C. Schouten, *Catal. Today* 57 (2000) 143.
- [4] M. Besson, P. Gallezot, *Catal. Today* 57 (2000) 127.
- [5] T. Mallat, A. Baiker, *Catal. Today* 24 (1995) 143.

- [6] T. Mallat, A. Baiker, *Top. Catal.* 8 (1999) 115.
- [7] D. Ferri, T. Bürgi, A. Baiker, *J. Phys. Chem. B* 105 (2001) 3187.
- [8] C. Keresszegi, T. Bürgi, T. Mallat, A. Baiker, *J. Catal.* 211 (2002) 244.
- [9] A.P. Markusse, B.F.M. Kuster, D.C. Koningsberger, G.B. Marin, *Catal. Lett.* 55 (1998) 141.
- [10] H.H.C.M. Pinxt, B.F.M. Kuster, D.C. Koningsberger, G.B. Marin, *Catal. Today* 39 (1998) 351.
- [11] I.J. Shannon, T. Maschmeyer, G. Sankar, J.M. Thomas, R.D. Oldroyd, M. Sheehy, D. Madill, A.M. Waller, R.P. Townsend, *Catal. Lett.* 44 (1997) 23.
- [12] D. Bazin, H. Dexpert, J. Lynch, in: Y. Iwasawa (Ed.), *X-ray Absorption Fine Structure for Catalysts and Surfaces*, Vol. 2, World Scientific, Singapore, 1996, p. 113.
- [13] G. Sankar, J.M. Thomas, R.A. Catlow, *Top. Catal.* 10 (2000) 255.
- [14] J.-D. Grunwaldt, B.S. Clausen, *Top. Catal.* 18 (2002) 37.
- [15] B.S. Clausen, H. Topsøe, R. Frahm, *Adv. Catal.* 42 (1998) 315.
- [16] M.A. Newton, A.J. Dent, J. Evans, *Chem. Soc. Rev.* 31 (2002) 83.
- [17] T. Ressler, *J. Synchrotron Radiat.* 5 (1998) 118.
- [18] C. Keresszegi, T. Mallat, A. Baiker, *New J. Chem.* 25 (2001) 1163.
- [19] T. Mallat, Z. Bodnar, P. Hug, A. Baiker, *J. Catal.* 153 (1995) 131.