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Comparative *in situ* XAS investigations during aerobic oxidation of alcohols over ruthenium, platinum and palladium catalysts in supercritical CO_2

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Abstract

The aerobic oxidation of benzyl alcohol to benzaldehyde in supercritical carbon dioxide was performed over alumina supported platinum and ruthenium catalysts, and the results were compared to those obtained over a Pd/Al_2O_3 catalyst. Despite of similar reaction conditions and although comparable activities have been reported in liquid solvents, the catalytic performance over Pt- and Ru-based catalysts was significantly lower than on the palladium catalyst. *In situ* monitoring of the catalyst structure by X-ray absorption spectroscopy during the activation procedure (reduction of the catalyst by hydrogen) uncovered a different reduction behaviour of these catalysts compared to the palladium one: to achieve a complete reduction of the noble metal particles a higher temperature had to be applied in case of Pt and Ru. *Operando* XAS studies during benzyl alcohol oxidation also revealed a rather different redox behaviour of Ru: under stoichiometric reaction conditions the Ru particles were oxidized to a large extent, which is probably at the origin of the low catalytic activity. Instead, the platinum catalyst showed a similar redox behaviour to palladium. However, *in situ* ATR-IR spectroscopy revealed an enhanced formation and adsorption of carbonaceous species including carbon monoxide on the Pt-surface. In case of Pd-based catalysts the higher redox-stability and the effective removal of carbonaceous species in the presence of oxygen are suggested to be key factors contributing to the high reaction rates observed during the oxidation of benzyl alcohol.

Keywords: Alcohol oxidation; *Operando* spectroscopy; *In situ* X-ray absorption spectroscopy; Infrared spectroscopy; Supercritical fluids; Carbon dioxide

1. Introduction

The partial oxidation of alcohols to aldehydes and ketones is an important class of reactions in the fine chemistry industry. These reactions have traditionally been performed applying stoichiometric amounts of inorganic oxidants, but nowadays there is a strong need to develop new and environmentally benign methods [1–4]. A well established alternative approach is the liquid phase oxidation of alcohols with molecular oxygen in the presence of a solid catalyst, resulting in environmentally friendly processes [1–9]. The most commonly used catalysts consist of platinum, palladium, ruthenium, rhodium on carbon or alumina as support. Bi- or multimetallic catalysts are generally more selective and especially more resistant to deactivation than monometallic catalysts. Typically Bi or Pb are used as promoters for platinum and palladium [1–3,6,10], whereas ruthenium and rhodium are applied without promoters [11–15]. In case of water insoluble alcohols, the use of supercritical carbon dioxide as an alternative ‘‘green’’ solvent (cf. e.g. Refs. [16–19]) has recently been successfully proposed, avoiding the use of detergents or organic solvents [20,21]. In some cases higher reaction rates than in conventional liquid solvents with comparable selectivities and improved catalysts lifetime were reported [22–26]. In our previous work, we investigated the aerobic oxidation of benzyl alcohol to benzaldehyde in supercritical carbon dioxide over a palladium supported catalyst. We showed that by optimization of the reaction conditions a very high reaction rate (one order of magnitude higher than in liquid phase) with a constant selectivity to benzaldehyde (*ca.* 95%) could be achieved [23]. The phase behaviour of the reaction mixture [25,27] and the oxidation state of the solid catalyst [28,29] were found to be crucial for the high catalytic activity. In particular, we showed that the reaction could be effectively investigated, understood

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and optimized only by applying the appropriate *in situ* spectroscopic techniques (combined transmission IR/ATR-IR and X-ray absorption spectroscopy). This resulted also in a deeper understanding of the advantages and limitations of supercritical CO_2 in heterogeneous catalysis and underlined the necessity of *in situ* spectroscopic studies in catalysis not only at normal pressure [30–34], but even under the demanding conditions of supercritical fluids [35,36].

Here we extended these studies to ruthenium and platinum supported catalysts, which are generally successfully used in liquid phase oxidation [9]. However, their application in the aerobic oxidation of alcohols in supercritical CO_2 has not been widely investigated up to now. The selective oxidation of 1- and 2-propanol over platinum supported catalysts was studied by Gläser et al. [22]. Campestrini et al. reported on the application of immobilized ruthenium catalysts during the selective oxidation of different benzyl and alkyl alcohols in supercritical CO_2 [37]. In the present work we applied two commercially available catalysts, platinum and ruthenium supported on alumina. They were tested during the selective oxidation of benzyl alcohol as a model reaction. Catalytic experiments were performed in a continuous-flow fixed-bed reactor focusing on the influence of the main process variables on rate and selectivity. *Operando* XAS investigations were performed to gain insight into the activation of the catalysts by reduction with hydrogen as well as into their behaviour during the aerobic oxidation of benzyl alcohol. Based on these investigations correlations between structure and activity should be uncovered. Finally the results are compared to those obtained with a palladium catalyst.

2. Experimental

2.1. Catalytic measurements

The reactions were performed isothermally in a fixed-bed stainless steel tubular reactor with an inner diameter of 13 mm and 38 ml volume. The temperature of the catalyst bed was monitored by means of an axially movable thermocouple placed in the center of the reactor. Three commercial shell impregnated catalysts were used: 0.5 wt% Pd/Al_2O_3 (Engelhard 4586, BET surface area 96 $m^2\,g^{-1}$, dispersion of 29%), 0.5 wt% Pt/Al_2O_3 (Engelhard 4751, BET surface area 81 $m^2\,g^{-1}$, dispersion of 36%) and 0.5 wt% Ru/Al_2O_3 (Engelhard 4871, BET surface area 96 $m^2\,g^{-1}$, dispersion of 7%). They were crushed and used as a sieved fraction (*ca.* 0.5–1.4 mm) together with pure alumina (Engelhard 43299) of the same sieved fraction, which was used to dilute the catalyst bed to avoid possible hot spot formation by the exothermic reaction. 2.5 g of catalyst and 1.5 g of alumina were loaded, corresponding to a bed length of *ca.* 4 cm. Glass beads were placed above the catalyst to ensure an optimal distribution of the reactants at the beginning of the catalytic bed. As an activation step, the catalyst was pre-reduced *in situ* with 5%H_2/N_2 before starting the measurements. The reduction temperature was 100 °C for the Pd catalyst, and 100 or 180 °C for the Ru and Pt catalysts (cf. the following sections). The heating rate was 6 °C/min, and the catalyst was hold at the desired reduction temperature for 1 hour. Benzyl alcohol (Fluka, 13160, purity >99.0%) was dosed by a Gilson 305 HPLC pump and oxygen (Pangas, purity $\geq$ 99.999%) was supplied to the reactor through a six-port valve (Rheodyne, model 7000) dosing 0.05 ml or 1 ml pulses at a pressure of 160–190 bar and constant frequency. A constant pressure over the catalyst bed was maintained by a pressure regulator for CO_2, and the total gas flow was controlled at the vent. Quantitative results were obtained via GC analysis (HP-6890, FFAP column). The minimum conversion that can be reliably detected is at about 2%; traces can be detected down to about 0.5%. The main by-products are benzoic acid and benzyl benzoate. Details on the experimental setup can be found in Refs. [20,23].

2.2. XAS experiments

Operando XAS experiments were performed in transmission mode in a specially constructed *in situ* spectroscopic flow cell. The cell has a stainless steel body and it is equipped with beryllium windows that allow the X-ray beam to penetrate. The catalyst is loaded inside the cell as a sieved fraction of crushed pellets. Therefore the spectroscopic cell works as a fixed-bed continuous-flow catalytic reactor, thus warranting optimal conditions for the simultaneous monitoring of both the catalyst structure by XAS and the catalytic activity by GC. The catalyst and the substrate/solvents utilized during the *operando* XAS measurements were the same as used during the catalytic experiments in the conventional reactor, and the experimental setup was kept as close as possible to that in the home laboratory for the conventional catalytic tests. Details on the *in situ* cell and on the experimental setup can be found in Refs. [28,29].

Operando XAS investigations at the Pd K-edge and Ru K-edge were performed at beamline X1 at HASYLAB (DESY, Hamburg) using a Si(3 1 1) double crystal monochromator. Experiments at the Pt L_3-edge were performed at the ANKA-XAS beamline (ANKA, Karlsruhe) using a Si(1 1 1) double crystal monochromator. In both cases the crystals were slightly detuned to minimize higher harmonics and three ionization chambers were used to record the intensity of the incident and transmitted X-ray. Pd and Pt foils and a pellet of $RuCl_3$ were used for energy calibration. EXAFS spectra were recorded around the Pd K-edge in the step scanning mode between 24,000 and 25,800 eV, around the Ru K-edge between 21,880 and 22,880 eV, and around the Pt L_3-edge between 11,415 and 12,540 eV. The raw data were energy-calibrated, background corrected, normalized and smoothed using the Athena 0.8.049 software [38]. The k^3-weighted EXAFS spectra at the Pd K-edge, at the Ru K-edge and at the Pt L_3-edge were Fourier transformed in the interval $k = 2.0–13$ Å^{-1}. The k^1-weighted EXAFS spectra at the Ru K-edge was Fourier transformed in the interval $k = 2.0–12$ Å^{-1}.

2.3. ATR-IR experiments

In situ ATR-IR investigations were carried out in a custom-made stainless steel high-pressure view cell described in detail in Ref. [39]. The view cell is equipped with an internal reflection element (IRE) at the bottom (ZnSe-crystal) and ZnSe windows for transmission IR at the top of the cell. Fourier transformed infrared spectra were recorded with a Bruker IFS-66/S FT-IR spectrometer equipped with a liquid nitrogen-cooled MCT detector, accumulating 200 scans at a resolution of 4 cm^{-1}. To gain information on the changes on the catalyst surface the IRE was coated with a thin catalytic layer. Two different kind of catalyst have been used for this purpose: 5 wt% Pd/Al_2O_3 (Johnson-Matthey, 324) and 5 wt% Pt/Al_2O_3 (Engelhard, 4759). To coat the IRE, 4 mg of catalyst powder were suspended in 0.4 ml water. The suspension was put onto the crystal, which was then dried at RT in air. The experiments were performed in a similar fashion to those described in Ref. [25]. At first the catalyst was reduced *in situ* by pure hydrogen, then the cell was loaded with the proper amount of benzyl alcohol and CO_2, and finally the temperature and the pressure were adjusted to the desired values. Oxygen was added during the experiment by feeding it from a line at 180 bar.

3. Results

3.1. Catalytic investigations

In previous studies, we reported that benzyl alcohol could be oxidized by molecular oxygen in $scCO_2$ over 0.5 wt% Pd/Al_2O_3 with high selectivity (>95%) and high reaction rates ($>1500\ mol_{product}\ mol_{Pd}^{-1}\ h^{-1}$) if the pressure was high enough (>100 bar) and the temperature above 70 °C [23,25]. According to reports on alcohol oxidation in liquid phase, also Pt- and Ru-based catalysts should be effective catalysts in the reaction [9], prompting us to study the activity of 0.5 wt% Ru/Al_2O_3 and 0.5 wt% Pt/Al_2O_3 during oxidation of benzyl alcohol for comparison. Similarly as the palladium catalyst, the Ru and Pt catalysts were received in the form of shell-impregnated cylindrical pellets (3.2 mm diameter and height) and used as a sieved fraction (*ca.* 0.5–1.4 mm). After pre-reduction in hydrogen at 100 °C, they were tested in the continuous flow reactor under similar reaction conditions as those applied in the studies with the palladium catalyst (cf. Section 2). Some representative results of the catalytic tests are reported in Table 1. Experiments at standard conditions (150 bar, 80 °C, 1 mol% benzyl alcohol, 0.5 mol% oxygen, 0.233 mol/min CO_2, entries 1–3 in Table 1) showed a remarkably lower activity of the platinum and ruthenium catalysts. Whereas the palladium-based catalyst afforded a conversion of nearly 50%, the conversion under the same conditions was below the detection limit over 0.5 wt% Pt/Al_2O_3 and 0.5 wt% Ru/Al_2O_3. The conversion over platinum and ruthenium could only be increased by raising the temperature and the oxygen concentration (entries 6–13 in Table 1). However, the reaction rate remained far below the one achieved with palladium, which could also be increased either by adding more oxygen (entries 14–16, recorded with a CO_2 flow rate of 0.1 mol/min to rule out phase behaviour effects [23]) or increasing the temperature (entries 1, 17, 18). Hence, we can conclude that palladium shows superior catalytic performance in benzyl alcohol oxidation in supercritical CO_2 than platinum and ruthenium. Nevertheless good catalytic activities have been reported for 1- and 2-propanol oxidation in $scCO_2$ [22] as well as in liquid phase [2,7,9,40,41]. Shedding more light on possible reasons for the lower catalytic activity of platinum and ruthenium catalysts requires *in situ* spectroscopic studies. In the present work, we applied X-ray absorption spectroscopy to investigate the structure of the solid catalysts during the activation procedure and under reaction conditions.

Table 1
Catalytic results during the selective oxidation of benzyl alcohol in $scCO_2$ over different alumina-supported noble metal catalysts and under different reaction conditions; 2.5 g of catalyst diluted with alumina and pre-reduced at 100 °C in hydrogen were used; metal loading of all catalysts 0.5 wt%

Entry	Catalyst	T (°C)	P (bar)	Alcohol (mol%)	O_2 (mol%)	Conversion (%)	Selectivity (%)
1	Pd/Al_2O_3	80	150	1	0.5	48.3	94.7
2	Pt/Al_2O_3	80	150	1	0.5	–[a]	–[a]
3	Ru/Al_2O_3	80	150	1	0.5	–[a]	–[a]
4	Pt/Al_2O_3	80	120	1	0.5	–[a]	–[a]
5	Ru/Al_2O_3	80	120	1	0.5	–[a]	–[a]
6	Pt/Al_2O_3	80	150	1	2	1.2	100
7	Pt/Al_2O_3	80	150	1	5	1.7	100
8	Pt/Al_2O_3	140	150	1	0.5	4.1	100
9	Pt/Al_2O_3	140	150	1	2	6.5	100
10	Pt/Al_2O_3	140	150	1	5	10.7	98.7
11	Pt/Al_2O_3	140	120	1	0.5	2.8	100
12	Ru/Al_2O_3	120	150	1	0.5	3.0	100
13	Ru/Al_2O_3	140	150	1	0.5	5.4	100
14	Pd/Al_2O_3	80	150	1.9	0.95	38	95.8
15	Pd/Al_2O_3	80	150	1.9	1.9	46.5	94.2
16	Pd/Al_2O_3	80	150	1.9	5.5	52.8	93.8
17	Pd/Al_2O_3	60	150	1	0.5	16.3	96.0
18	Pd/Al_2O_3	70	150	1	0.5	26.5	95.6

[a] Below detection limit of GC.

3.2. Monitoring of the solid catalysts during reduction with hydrogen

Firstly, we investigated the reduction behavior of the catalysts by hydrogen, which is used as activation step in the conventional laboratory experiments. The results are shown in Fig. 1. Interestingly, upon heating of the catalysts in a hydrogen/helium flow and simultaneous monitoring of the catalyst structure by XAS, changes in the XANES region of both Ru (Fig. 1a) and Pt (Fig. 1c) were observed until 180 °C. A further increase of the temperature did not have any effect on the structure. Therefore, we can conclude that at 100 °C the catalysts are not fully reduced. An almost full reduction of the metal constituent of the catalysts by hydrogen was achieved at 180 °C, as also confirmed by the similarities with the reference spectra shown in Fig. 1b and d. Instead, experiments performed with the palladium catalyst (Fig. 1e) showed that already at room temperature the catalyst could be partly reduced in hydrogen, and at 80 °C the reduction was complete (cf. the reference spectra in Fig. 1f).

These results indicate that the activation procedure (reduction in hydrogen at 100 °C) prior to the catalytic tests,

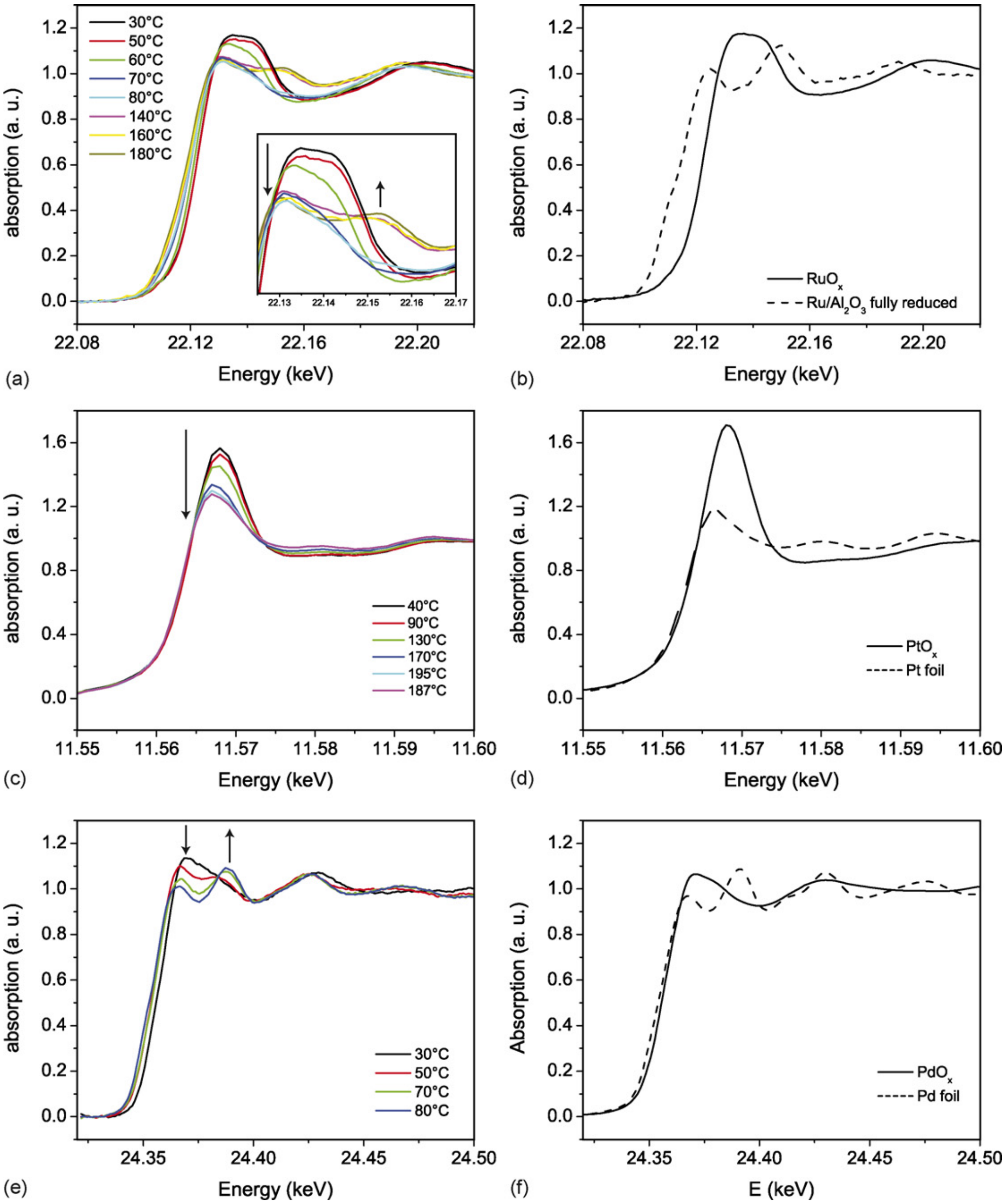

Fig. 1. XANES spectra recorded *in situ* during reduction of the catalysts in a 5% H_2/He flow while heating up from room temperature to 180 °C: (a) 0.5 wt% Ru/Al_2O_3, spectra recorded at the Ru K-edge, in the inset the region close to the adsorption edge is magnified for a better visualization of the changes; their trend is indicated by the arrows; (c) 0.5 wt% Pt/Al_2O_3, spectra recorded at the Pt L_3-edge, the arrow indicates the trend of the change of the Pt whiteline; (e) 0.5 wt% Pd/Al_2O_3, spectra recorded at the Pd K-edge, the arrows indicate the trend of the changes in the XANES features; reference spectra for comparison in plots (b), (d) and (f).

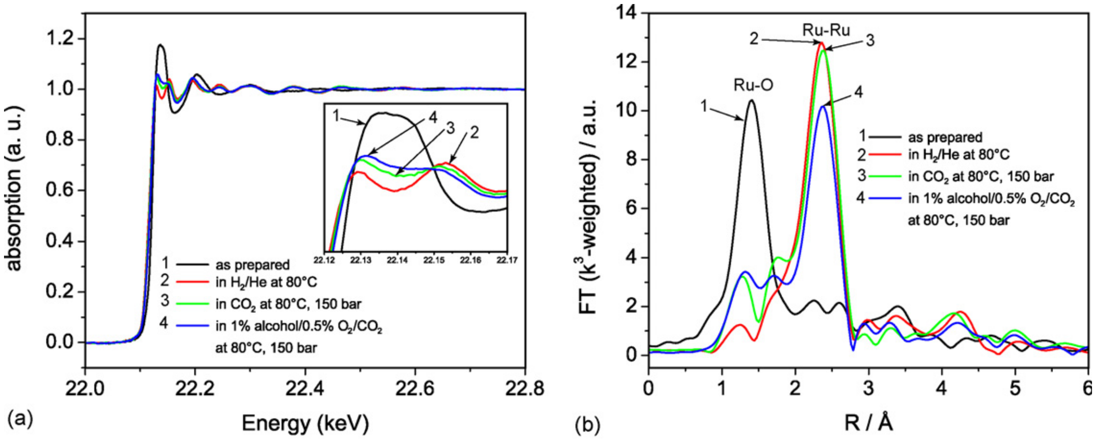

Fig. 2. EXAFS spectra at the Ru K-edge (a) and corresponding Fourier transformed EXAFS spectra (b) recorded in an *operando* spectroscopic cell during aerobic oxidation of benzyl alcohol over 0.5 wt% Ru/Al_2O_3 under different reaction conditions; details in text.

was not sufficient to fully reduce the ruthenium and platinum catalysts, in contrast to observations with the palladium catalyst. Therefore, further catalytic investigations in the conventional fixed-bed reactor were performed after pre-reduction of the ruthenium and platinum catalysts at a temperature of 180 °C. The results (not shown) still showed for both Ru and Pt catalysts a low catalytic activity, with an alcohol conversion at 80 °C below the detection limit of the GC.

3.3. Operando XAS investigations during aerobic benzyl alcohol oxidation in $scCO_2$

In a second step, the structure of the catalysts pre-reduced in hydrogen (at 180 °C for 0.5 wt% Pt/Al_2O_3 and 0.5 wt% Ru/Al_2O_3 and at 80 °C for 0.5 wt% Pd/Al_2O_3, cf. previous section) was investigated by XAS during the aerobic oxidation of benzyl alcohol in supercritical CO_2. The experiments were performed in a similar way to those previously reported with a palladium catalyst, applying a similar experimental setup, which allows the simultaneous monitoring of the structure of the catalysts and their catalytic performance (cf. Section 2 and Refs. [28,29]). During the experiments with the palladium catalyst the reaction rate measured in the *in situ* XAS flow cell was 1890 $mol_{product}\ mol_{Pd}^{-1}\ h^{-1}$ (80 °C, 150 bar, 1.9 mol% alcohol, 1.9 mol% O_2 0.1 mol/min CO_2). This is similar to the reaction rate measured in the conventional reactor (1760 $mol_{product}\ mol_{Pd}^{-1}\ h^{-1}$), underlining the good flow and mixing properties of the spectroscopic cell. However, note that only in the case of the Pd/Al_2O_3 catalyst high reaction rates were observed (Table 1). Due to the small amount of catalyst loaded in the XAS cell (*ca.* 0.5 g versus 2.5 g in the conventional reactor) the lowest activity which can be measured is at about 2% of conversion, corresponding to a reaction rate of 300 $mol_{product}\ mol_{Pd}^{-1}\ h^{-1}$. The reaction rates expected with Ru and Pt catalysts are lower than this threshold limit (cf. Table 1), and therefore no direct information on the catalytic activity can be extracted during the EXAFS measurements. However, since the catalysts, the experimental setup and the reaction conditions applied during the XAS investigations were exactly the same as those used during benzyl alcohol oxidation in the conventional reactor, the experiments can also in this case be considered truly *operando*.

The XANES and EXAFS spectra recorded during oxidation of benzyl alcohol over the ruthenium catalyst are shown in Fig. 2. The ruthenium constituent at 80 °C in a hydrogen/helium flow is in an almost fully reduced state (spectrum 2 in Fig. 2, compared to spectrum 1, which is the as-prepared catalyst before the reduction treatment at 180 °C). By adding CO_2 at 80 °C and 150 bar, changes mainly in the XANES region were observed (cf. spectrum 2 and 3 in Fig. 2a). By adding benzyl alcohol (1 mol%) and oxygen (0.5 mol%) a significant change in the bulk structure of the catalyst was observed, as reflected by the changes in the Fourier transformed EXAFS spectra (cf. spectrum 3 and 4 in Fig. 2b). Both the changes in the XANES spectra (decrease of the feature at 22.15 keV, Fig. 2a) and in the Fourier transformed EXAFS spectra (decrease of the Ru–Ru backscattering at 2.36 Å) indicate the adsorption and incorporation of oxygen, resulting in an oxidation of the ruthenium particles. The oxidized catalyst could be partially re-reduced by benzyl alcohol, but only at 180 °C and without oxygen in the feed. In Fig. 3, the corresponding Fourier transformed EXAFS spectra (k^1-weighted, for better visualization of the variation of the Ru–O backscattering) are shown. Obviously, at 180 °C and without oxygen in the feed, a decrease of the Ru–O peak was observed together with an increase of the Ru–Ru peak, indicating the re-reduction of the metallic particles, even though not to the same extent as observed with the catalyst in the H_2/He flow at 80 °C (dotted spectrum in Fig. 3).

The results obtained during benzyl alcohol oxidation over the platinum catalyst are shown in Fig. 4. At 80 °C in a H_2/He flow the platinum particles are fully reduced (spectrum 2 in Fig. 4a–c, spectrum 1 is the as-prepared catalyst before reduction at 180 °C). By adding CO_2 at 80 °C and 150 bar and subsequently benzyl alcohol (1 mol%) and oxygen (0.5 mol%) in CO_2, hardly any change in the catalyst structure was observed (cf. spectra 3 and 4 in Fig. 4a–c). Instead a remarkable oxidation of the platinum constituent was observed by increasing the oxygen concentration in the feed to 5 mol%, which was accompanied by an activity increase (cf. entries 6, 7

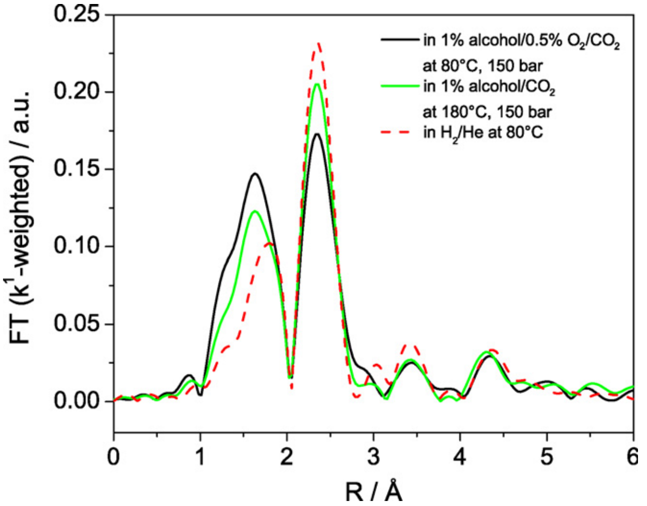

Fig. 3. Fourier transformed k^1-weighted EXAFS spectra at the Ru K-edge recorded during aerobic oxidation of benzyl alcohol over 0.5 wt% Ru/Al_2O_3 showing the re-oxidation of the catalyst under reaction conditions at 80 °C and the reduction by the alcohol at 180 °C.

and 9, 10 in Table 1). The oxidation of the platinum particles is especially visible in the Fourier transformed spectrum 5 in Fig. 4b, indicated by the decrease of the Pt–Pt backscattering at 2.55 Å. By increasing the temperature to 140 °C and decreasing the oxygen concentration to stoichiometric conditions (1 mol% alcohol, 0.5 mol% O_2 in CO_2 at 150 bar) the platinum catalyst could be slightly re-reduced. For a better visualization of the changes in the XANES region under different reaction conditions the $\Delta\mu$ difference technique has been applied, which has been successfully utilized in literature for investigating the adsorption of hydrogen, oxygen and CO on small supported platinum particles [42–44]. The spectrum of the fully reduced particles (recorded at 80 °C in H_2/He, spectrum 2 in Fig. 4a–c) served as a reference for the subtraction. The results are shown in Fig. 4d. A clear trend could be observed, and the feature at *ca.* +3 eV increased by rising the oxygen concentration (spectra 4 and 5 in Fig. 4d), as also confirmed by the spectrum recorded in an O_2/CO_2 flow (spectrum marked with an asterisk).

The behaviour of the platinum catalyst is similar to that observed with a palladium catalyst: by increasing the oxygen concentration in the feed the palladium constituent is partially oxidized, as uncovered by the changes in the XANES region (Fig. 5a) and by the decrease of the Pd–Pd backscattering peak in the FT EXAFS spectra (Fig. 5b). Particularly, using an oxygen concentration of 5.5 mol% in the feed (alcohol concentration 1 mol%, spectrum 3 in Fig. 5), the palladium constituent is in a partially oxidized state, as here also observed with the platinum catalyst (spectrum 5 in Fig. 4a–c). The

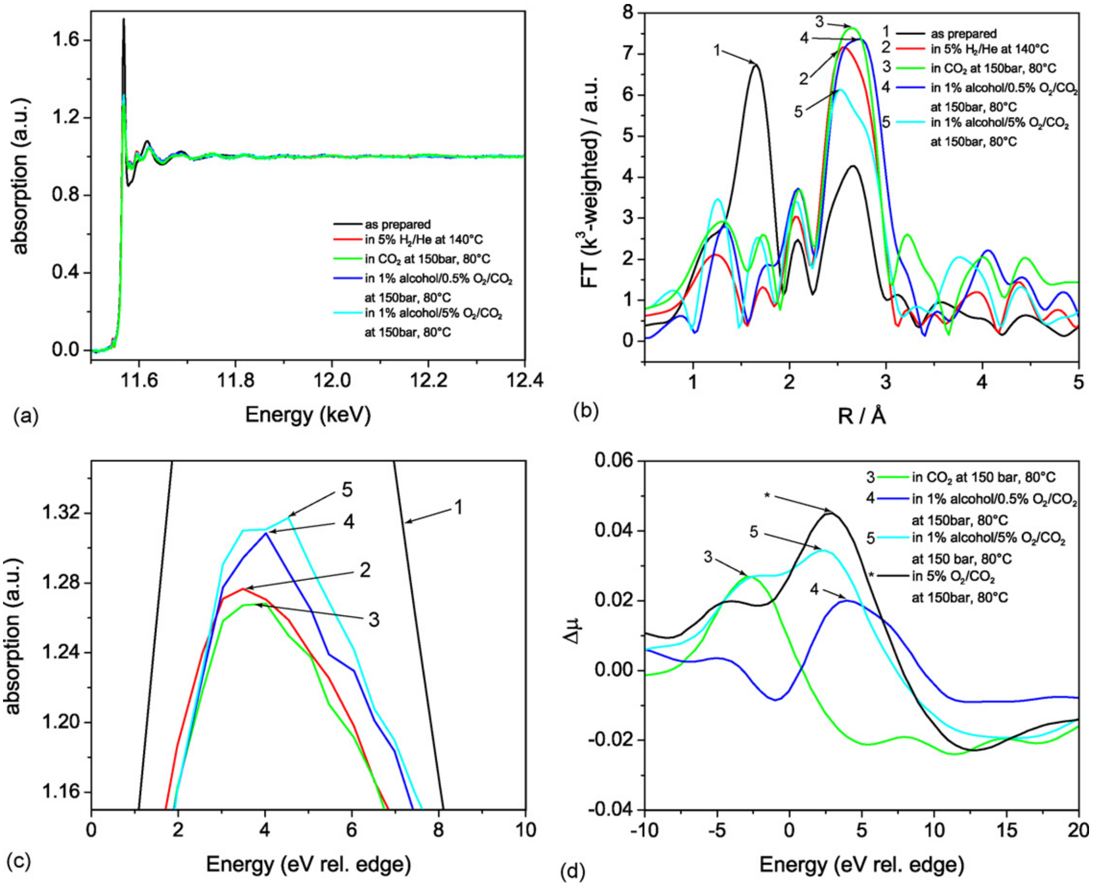

Fig. 4. EXAFS spectra at the Pt L_3-edge (a) and corresponding Fourier transformed EXAFS spectra (b) recorded during aerobic oxidation of benzyl alcohol over 0.5 wt% Pt/Al_2O_3 under different reaction conditions; in graphic (c) a zoom in the region of the Pt whiteline is shown; in graphic (d) the spectra at the Pt L_3-edge are analyzed applying the $\Delta\mu$ difference technique; details in text.

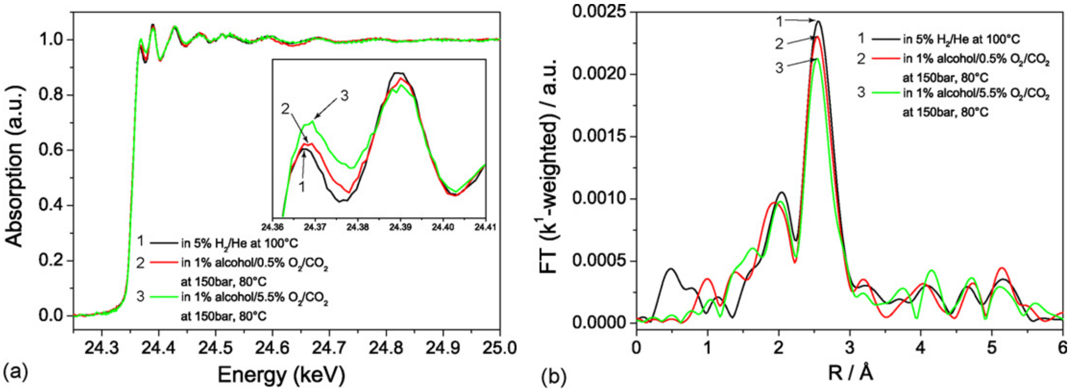

Fig. 5. EXAFS spectra at the Pd K-edge (a) and corresponding Fourier transformed k^1-weighted EXAFS spectra (b) recorded in an *operando* spectroscopic cell during aerobic oxidation of benzyl alcohol over 0.5 wt% Pd/Al_2O_3 under different reaction conditions.

catalytic activity measured during the *operando* XAS experiments was in-line with the results obtained in the conventional reactor, and during benzyl alcohol oxidation over a palladium catalyst an increase of the reaction rate was observed upon raising the oxygen concentration.

3.4. In situ ATR-IR investigations

In situ ATR-IR investigations were performed during benzyl alcohol oxidation over both platinum and palladium catalysts in order to shed some light on the phenomena taking place at the catalyst/fluid interface. Catalysts with higher metal loading (5 wt%, cf. Section 2) were chosen in order to increase the sensitivity towards the noble metal and to accelerate the overall reaction rate. The experiments were performed as described in the experimental section, and oxygen was added only when the desired temperature and pressure were reached and the phase behaviour showed stationary conditions. The aim of this strategy was to investigate the formation and adsorption of carbonaceous species including carbon monoxide before and after the oxygen addition. In Fig. 6a, the ATR-IR spectra are shown. The phase behaviour inside the catalyst pores was similar for both platinum and palladium catalysts and did not significantly change upon addition of oxygen. Single phase conditions were observed in both cases, with the alcohol hardly detectable due to the short probing path of the ATR-IR technique [25]. The only differences between Pd and Pt were observed in the asymmetric stretching band of CO_2 at 2336 cm^{-1} (more intense in the case of Pd, indicating a different density inside the catalyst pores, probably due to a different pore geometry [45]) and in the ν_2 vibration (bending mode) of water around 1600 cm^{-1}, more marked in the case of Pt. For a better identification of the changes induced on the catalyst surface upon addition of oxygen, the spectra recorded without and with O_2 were subtracted, and the results are shown in Fig. 6b. In the case of the platinum catalyst it was possible to uncover a weak band at 2026 cm^{-1}, which could be attributed to adsorbed CO [46], whereas hardly any bands due to adsorbed CO could be found for the Pd catalyst. This evidences that the degradation of benzaldehyde on Pt-particles occurs much faster than on the Pd-particles. After the addition of oxygen, the reaction started in both cases (not shown) and it could be effectively monitored by transmission IR spectroscopy, similarly as in Ref. [25]. The results confirmed the observations in the fixed-bed continuous-flow reactor indicating a much faster reaction in the case of the Pd catalyst.

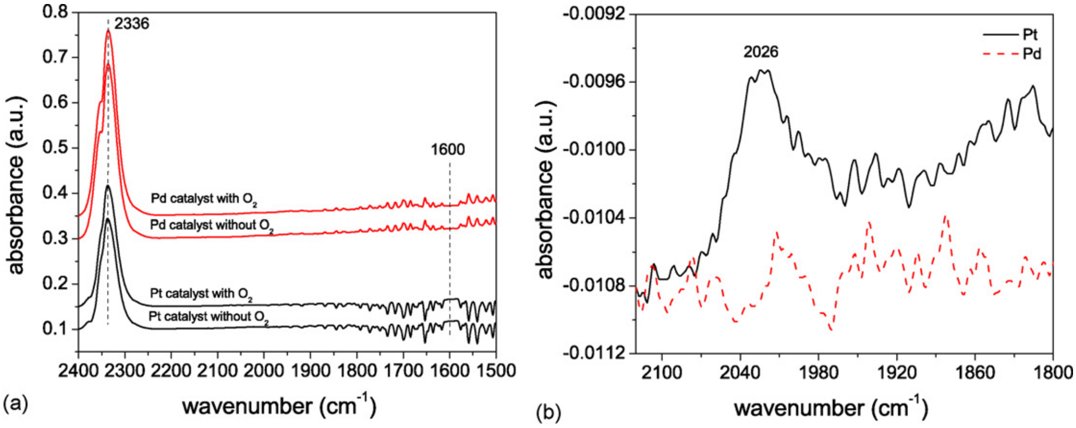

Fig. 6. *In situ* ATR-IR spectra recorded at the catalyst/fluid interface of a 5 wt% Pd/Al_2O_3 and 5 wt% Pt/Al_2O_3: (a) spectra recorded at 80 °C, 150 bar, 1 mol% alcohol in CO_2 before and after the addition of O_2 (1.4 mol%); (b) spectra obtained by subtracting the one in the presence of oxygen from the one without oxygen; details in text.

4. Discussion

We compared the selective oxidation of benzyl alcohol with molecular oxygen in supercritical carbon dioxide over ruthenium and platinum supported catalysts to that over Pd-based catalysts. Catalytic tests performed in a conventional fixed-bed reactor showed remarkably lower reaction rates than the ones observed over palladium catalysts under similar reaction conditions [23,25]. Using the conditions of 150 bar, 80 °C, 1 mol% alcohol, 0.5 mol% O_2 in CO_2 a reaction rate above 1500 $mol_{product}\ mol_{Pd}\ h^{-1}$ (alcohol conversion around 50%) was achieved over Pd/Al_2O_3, whereas over Ru/Al_2O_3 and Pt/Al_2O_3 the alcohol conversion was below the detection limit of GC (cf. Table 1). The maximum rate for the Pt/Al_2O_3 catalyst was 660 $mol_{product}\ mol_{Pt}\ h^{-1}$ and for Ru/Al_2O_3 170 $mol_{product}\ mol_{Ru}\ h^{-1}$. For the three catalysts investigated the metal loading was the same (0.5 wt%), the structural properties identical (sieved fraction of crushed shell impregnated pellets), and the characteristics of the catalytic bed very similar (resulting in very similar flow conditions in the reactor). Therefore, these factors cannot be responsible for the lower catalytic activity measured over the ruthenium and platinum catalysts. The phase behaviour of the reaction mixture is known to play a crucial role for a high catalytic activity in many reactions in supercritical fluids, since it strongly affects the mass transfer [35,47]. Also the selective oxidation of benzyl alcohol was found to be strongly dependent on the phase behaviour [23,25]. However, the phase behaviour can be excluded as a possible cause of the low catalytic activity since experiments performed under the same reaction conditions (resulting in identical phase behaviour) but over different catalysts resulted in different reaction rates (e.g. entries 1–3 in Table 1). Additional *in situ* ATR-IR investigations uncovered that also the phase behaviour inside the catalyst pores is similar for platinum and palladium catalysts (cf. Fig. 6a), which therefore cannot be responsible for the differences in the catalytic activity.

Another crucial factor during aerobic oxidation of alcohols is the oxidation state of the noble metal under reaction conditions. In fact, from oxidation in liquid phase it is well known that alcohol oxidation takes place via a dehydrogenation mechanism over a reduced metal particle, and that a deactivation takes place when the oxygen supply to the active site is faster than its consumption, thus resulting in the formation of a layer of inactive surface oxide [1,3,6,9,48]. This is one of the most frequently observed causes for catalyst deactivation during aerobic alcohol oxidation in liquid phase, and recently we proved that it plays a crucial role also during the Pd-catalysed oxidation of alcohols in supercritical CO_2 [28,29].

Extending these studies also to ruthenium and platinum catalysts is therefore obvious, but especially for *operando* XAS investigations at the Pt L_3-edge the spectroscopic cell and experimental setup had to be modified. Due to the lower energy, the absorption of the X-ray beam by the beryllium windows of the cell and particularly by the dense CO_2 is more significant (cf. Ref. [36]). A catalyst with a higher metal loading than 0.5 wt% could not be used, in order to keep the noble metal particle size small. This guarantees that the technique is also sensitive to changes on the surface of the particles. Hence, a cell with thinner beryllium windows was developed, and during the experiments special care was put on the pressure and temperature stabilization (by adding extra pressure regulating valves and a pre-heater). The latter is fundamental to eliminate possible density changes of supercritical CO_2 which would be reflected in a variation of the X-ray absorption.

The investigation of the reduction behaviour uncovered that in contrast to the palladium catalyst, ruthenium and platinum required a higher temperature to be fully reduced by hydrogen (180 °C versus 80 °C, cf. Fig. 1). Nevertheless, the pre-reduction with hydrogen was not found to play a crucial role for the catalytic activity. Instead the high reduction temperature may be an indication of a different redox potential compared to the palladium catalyst. This may suggest that the dehydrogenation step (widely accepted as being the first step during alcohol oxidation over noble metal catalysts [9]) does not take place at low temperature on ruthenium and platinum particles, thus explaining the remarkably lower catalytic activity observed. Moreover, they may be faster re-oxidized, thus blocking the catalytically active sites for dehydrogenation.

The *operando* XAS investigations during alcohol oxidation over the ruthenium catalyst (cf. Figs. 2 and 3) confirmed this speculation. It was observed that already by exposing the catalyst to CO_2 a significant change in the electronic structure of Ru took place (cf. spectrum 3 in Fig. 2a) due to the adsorption of oxygen (present in traces in the carbon dioxide feed). Furthermore, under stoichiometric conditions of alcohol and oxygen, the metallic particles were remarkably oxidized on the surface (cf. spectrum 4 in Fig. 2b) and the catalyst (in the temperature range observed, i.e. up to 180 °C) could not be reduced by alcohol in the presence of oxygen, except if the oxygen feed was completely stopped (Fig. 3). This is a rather different behaviour in comparison to platinum and palladium catalysts, which are only to a much smaller extent oxidized under similar reaction conditions (cf. Figs. 2, 4 and 5). The slightly higher reaction rate at higher temperature (entries 3, 12, 13 in Table 1) may also be an indication of a faster dehydrogenation step, which results in a larger availability of surface hydrogen, contributing to keep the catalyst in a reduced state.

While the inferior activity of ruthenium may be attributed to its partial oxidation under reaction conditions, the lower activity of the platinum catalyst seems to be of different origin. In fact, the catalytic tests showed a better activity of this catalyst at higher oxygen concentration (entries 2, 6, 7 at 80 °C, and entries 8–10 at 140 °C in Table 1), and the *operando* XAS investigations clearly indicated that under the conditions of high oxygen concentration the platinum constituent was only in a partially oxidized state (cf. Fig. 4b). This behaviour is similar to that observed with the palladium catalyst (Fig. 5), where the palladium constituent was also found to be only partially oxidized under reaction conditions [28]. This observation is slightly different to that made in liquid phase [48], and it has been attributed to the altered mass transfer in supercritical fluids [29]. Thus, there are two possible explanations for the lower activity of the platinum catalyst. The platinum catalyst may be intrinsically less active in the reaction, even if it shows similar reduction/oxidation behaviour under reaction conditions. This is, however, surprising considering that in liquid phase alcohol oxidation platinum and palladium catalysts often perform in a similar way. Nevertheless, it has been reported that supported platinum particles are much more sensitive to the reaction conditions, and improvements can be achieved by the use of promoters [10]. From liquid phase oxidation it is also well known that already small amounts of carbon monoxide can block the Pt-surface and that there may be an easier decarbonylation pathway or a slower removal of carbonaceous species on Pt-based catalysts compared to Pd-based ones. The preliminary *in situ* ATR-IR study (cf. Fig. 6) suggests that a similar behaviour may also be encountered when performing oxidation in $scCO_2$, since the Pt catalyst showed a higher tendency to degradation of the aldehyde including the formation and adsorption of CO, at least under anaerobic conditions (cf. Fig. 6b). Moreover, the catalytic and spectroscopic experiments unraveled that under reaction conditions the platinum particles are only slightly oxidized (*operando* XAS, cf. Fig. 4) and that a higher catalytic activity is achieved at higher oxygen concentration in the feed (Table 1). This is probably beneficial for the removal of adsorbed CO and other carbonaceous species. However, in order to shed more light on their role and on the phenomena taking place at the catalyst/fluid interface further surface sensitive and *in situ* spectroscopic investigations are required. High pressure *in situ* infrared spectroscopy is a powerful technique, and its use is extremely promising since it may allow profound studies, similar to those performed in liquid phase (cf. e.g. [36,49]).

5. Conclusions

The aerobic oxidation of benzyl alcohol to benzaldehyde in supercritical carbon dioxide can be performed with higher reaction rates over palladium-based catalysts than over ruthenium and platinum ones. For the ruthenium-based catalyst, *operando* XAS investigations uncovered that after activation by pre-reduction the Ru-particles are re-oxidized under typical reaction conditions. The formed Ru-oxide layer on the top of the particles is probably less active than metallic noble metal sites. Instead, the lower activity of the platinum catalyst, which showed similar redox behaviour to the palladium one, cannot be traced back to the surface oxidation of the noble metal particles, and it is probably due to blocking of active sites by carbonaceous species and by a slow removal of adsorbed CO. Hence, the higher redox stability of the Pd-based catalyst and its lower propensity to catalyze the formation of carbonaceous species including carbon monoxide seem to lead to optimal properties during Pd-catalyzed alcohol oxidation in $scCO_2$, which may be achieved in the case of other noble metal supported particles only by using appropriate promoters.

This behaviour of ruthenium and platinum catalysts in $scCO_2$ is rather different to that observed during oxidation in liquid solvents. Nevertheless this is not unexpected since reactions in supercritical fluids often exhibit altered properties, including mass transport, oxygen solubility and phase composition. This implies that the knowledge gained at normal pressure and in conventional media cannot be directly transferred to reactions in supercritical fluids, which therefore require additional studies. For this purpose, *in situ* spectroscopy at high pressure is an inevitable tool. Therefore, in the future further efforts are needed to design optimal spectroscopic cells and appropriate setups to extend the applicability of other spectroscopic techniques to reactions in supercritical fluids or in general to reactions under the challenging conditions of high pressure, high temperature and non-gaseous fluid phases.

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