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Gold catalysed selective oxidation of alcohols in supercritical carbon dioxide

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The oxidation of benzyl alcohol to benzaldehyde over different supported gold catalysts in supercritical carbon dioxide has been investigated in a high-pressure batch reactor. Only molecular oxygen was used as oxidant and no base was needed. Different supports and preparation methods for the catalysts were tested and parameters like reaction temperature, pressure and molar ratios of the components were varied to study the catalytic behaviour. Gold colloids deposited on a titania support (1%Au/TiO_2) yielded a conversion of 16.0% after 3 h and a high selectivity to benzaldehyde of 99% under single-phase conditions. The reaction rate was significantly higher than in a corresponding "solvent-free" reaction without CO_2. Even higher rates were found when a CO_2-expanded phase was present. Monitoring of the oxidation in a high-pressure view cell via infrared transmission spectroscopy unravelled a slowdown of the reaction rate above 15% conversion. In addition, 1-octanol and geraniol were oxidised as well under similar conditions, yielding conversions of 4% and 10%, respectively, with selectivities towards octanal and geranial of 90% and 30%. Thus, the combined application of gold-based catalysts and supercritical CO_2 offers an interesting alternative to the known methods of alcohol oxidation.

KEY WORDS: alcohol oxidation; benzyl alcohol; 1-octanol; geraniol; gold catalysis; carbon dioxide; supercritical fluids; X-ray absorption spectroscopy.

1. Introduction

Apart from noble metals like palladium or platinum, also gold-based catalysts have recently been used for the heterogeneously catalysed oxidation of alcohols and hydrocarbons [1–3], which is both from an academic and an industrial point of view very attractive [1,4]. In spite of the lower reactivity of gold this approach can particularly yield higher selectivities than achieved over supported Pt or Pd catalysts [3,5–7]. Alcohol oxidation is typically performed in liquid phase. In case of water-soluble alcohols water can be used [8,9], but in case of gold catalysts the addition of a base is required [10–12]. Frequently, also organic solvents are applied. However, in an environmentally benign process, solvents should be minimised and simple oxidants should be used. Thus, solvent-free processes [7,11,13] in combination with simple and non-toxic oxidants like hydrogen peroxide and oxygen/air [4,8,11,13–17] attracted attention. But the reaction rates are typically lower, particularly since no base can be used [11,13]. An alternative approach is the employment of supercritical carbon dioxide[§] as an environmentally benign solvent, which was also recently used for selective alcohol oxidations [18–24]. In addition, since it allows performing the reaction in an inert and non-flammable medium at potentially high reaction rates [25–27], it provides several advantages from a process and catalytic point of view. By adjusting pressure and temperature the solvent and reactants can be assembled in a single reaction phase. Besides, the reaction can be performed in a CO_2-expanded reaction phase, where the oxygen solubility and the mass transport properties are still high [28,29]. In the present study we thus investigated the combination of these two concepts—gold catalyst and dense CO_2. We focused on the evaluation of the alcohol oxidation in the absence of an assisting base using supported gold catalysts and molecular oxygen as oxidant. The oxidation of benzyl alcohol was taken as a model reaction. Gold catalysts on different supports (titania, iron oxide and activated carbon) were prepared using different synthesis routes and were tested in a high-pressure batch reactor. With selected catalysts the influence of various reaction parameters and the extension of the approach to other, structurally different alcohols were investigated.

2. Experimental

2.1. Catalyst preparation

The catalyst preparation included deposition of gold colloids [30], impregnation and flame synthesis [31]. 1%Au/TiO_2(coll), 1%Au/Fe_2O_3(coll) and 1%Au/C(coll) were prepared via gold colloids by adding a colloidal solution of gold particles with a diameter of less than 4 nm (102 mL) to 100 mL of a suspension containing 2 g of the respective support. The support suspension

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[§] Note that the term "supercritical" in this paper is used for a reaction mixture exceeding the critical temperature of the solvent, despite several phases may be present.

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was stirred for 15 min at 750 rpm. Before adsorption of the colloids, the pH of both suspensions was adjusted to pH 2 by addition of sulfuric acid. Used supports were titania P25 (Degussa AG, BET surface area of 49 m^2/g) and activated carbon (ABCR, BET surface area of 1350 m^2/g). After stirring for 15 min, the resulting suspension was filtered and subsequently the filter cake was washed with water until the filtrate did not contain any chloride ions (checked by addition of $AgNO_3$(aq)). The solution of gold colloids was prepared similarly as described in ref. [30] by addition of 3.58 mL 28.84 mM $HAuCl_4$(aq) (ABCR, 51% Au) to a 100 mL flask containing 93.4 mL deionised water, 3 mL 1 M NaOH(aq) and 2 mL 0.95% aqueous solution of tetrakis(hydroxymethyl)phosphonium chloride (THPC) (Fluka, 80% in water). The colloidal solution was stirred for 15 min at 750 rpm before its addition to the support suspension. 1%Au/TiO_2(coll) was used as-prepared (dried at 80 °C for 15 h) and after calcination at 400 °C for 4 h. Another titania supported gold catalyst was prepared by impregnation of 1 g titania with 1.79 mL 28.84 mM $HAuCl_4$(aq) and drying at 80 °C for 10 h. The catalyst was used as-prepared (dried at 80 °C for 15 h) and after calcination at 400 °C for 4 h. In addition to 1%Au/Fe_2O_3(coll) an iron oxide supported gold catalyst was synthesised using flame spray pyrolysis [31,32]. For this purpose, a 0.25 M solution of Fe(III)acetylacetonate and a 1 mM solution of $HAuCl_4$, each in a 1 : 1 mixture of methanol and acetic acid were sprayed in a methane/oxygen flame. The parameters were similar to those reported in ref. [31].

2.2. Catalyst characterisation

The estimation of Au particle sizes and their dispersion was performed by scanning transmission electron microscopy (STEM) using a Tecnai F30 microscope (FEI, Eindhoven). To improve the *z*-contrast, high-angle annular dark field detection (HAADF-STEM) was employed. The particles were qualitatively analysed by energy dispersive X-ray spectroscopy (EDXS), for which the detector was attached to the Tecnai F30 microscope. The oxidation state of the particles was additionally determined by X-ray absorption spectroscopy (XAS) in fluorescence mode at the Swiss Norwegian beam line (SNBL) at ESRF (Grenoble, France). The spectra were recorded around the Au L_3-edge between 11.90 and 12.00 keV. The raw data were energy-calibrated, background corrected, normalised and smoothed using the WinXAS 3.0 software [33]. The surface area of the catalysts was calculated from the nitrogen adsorption isotherm according to the BET method.

2.3. Batch reactor experiments

The high-pressure batch reactor experiments were conducted in a 100 mL autoclave made of Hastelloy B (Premex Reactor AG, Lengnau). The liquid alcohol and the powdered catalyst were put in the reactor, which was then closed and linked to the gas lines. Oxygen (99.5%) was added at 23 °C until the appropriate pressure was reached. Finally, CO_2 (99.9%) was added with a compressor (NWA GmbH, Lörrach) from a CO_2 gas cylinder equipped with a dip tube. The amount was measured by a mass flow controller (RHE2, RHEONIK Messgeräte GmbH). The autoclave was heated to the reaction temperature (80–120 °C) and, after the respective reaction time, cooled down for half an hour by a water cooling system. Samples were taken by dissolving the reactor contents in 50 mL toluene (Fluka, puriss. p.a.). After filtration of the catalyst, the reaction mixture was injected in a gas chromatograph (HP 6800 series) equipped with FID detector and HP5 GC column (Agilent Technologies Inc., 25.0 m × 320 μm × 0.17 μm). The reactant composition of the standard experiment were 7 mmol of alcohol, 14 mmol oxygen and 1590 mmol CO_2. During repetitive experiments the conversion and selectivity could be reproduced with a margin of error of ±6% and ±0.4%, respectively.

To check for gold leaching the filtered solution was concentrated and the residue was dissolved in 10 mL aqua regia and diluted with deionised water. The samples were measured in a flame atomic absorption spectrometer (Varian SpectrAA 220FS) equipped with a Gold UltrAA HC lamp (Varian, λ_e = 242.8 nm). A gold AAS standard solution was used (Fluka, c(Au) = 1 g/L) for calibration. The detection limit was 1 μg/mL.

2.4. Phase behaviour studies and IR measurements

Phase behaviour studies were performed in a magnetically stirred high-pressure view cell with a variable volume of 22 mL to 62 mL [34]. In addition, a spectroscopic view cell was used [35], which was equipped with a digital camera for phase monitoring, ZnSe windows for transmission IR measurements and a ZnSe ATR crystal at the bottom of the cell. The crystal was coated with 8 mg of 1%Au/TiO_2(coll). The Fourier transform infrared (FT-IR) spectra were recorded with a Bruker IFS-66 spectrometer, equipped with an MCT detector. A detailed description of the setup can be found elsewhere [35]. Benzyl alcohol, oxygen and carbon dioxide were inserted in the same way as described above for the catalytic experiments.

2.5. Safety note

The experiments described in this paper involve the use of high pressure and require equipment with the appropriate pressure rating.

3. Results

Phase behaviour studies using video monitoring in a high-pressure view cell with sapphire window were used to discriminate the two-phase region and that with a single reaction phase. This allows to relate different catalytic performances of the reaction system at different pressures to the respective phase compositions. For this purpose, different mixtures of CO_2, O_2 and benzyl alcohol were investigated between room temperature and 120 °C and pressures up to 180 bar. Systems with an amount of both alcohol and oxygen < 1 mol%, a temperature of 80 °C and higher and a pressure above 140 bar consisted of a single phase, while deviations from these parameters towards lower CO_2 or higher oxygen amounts, lower temperature, and lower pressure yielded two phases (figure 1). The standard conditions for the conducted experiments were 0.4 mol% benzyl alcohol, 0.9 mol% oxygen, 98.7 mol% carbon dioxide and 0.1 g of catalyst. As figure 1a shows, only one phase was present.

Under these conditions different supports for gold colloids were tested: TiO_2, Fe_2O_3 and activated carbon (table 1). The size of the gold particles ranged from below 1 to 4 nm on TiO_2, from 1 nm to 5 nm on Fe_2O_3, and from 1 to 8 nm on carbon—as determined by HAADF-STEM measurements (figure 2). The average diameters were estimated with the aid of the STEM pictures to 1.9, 3.1 and 3.8 nm, respectively. The size of these particles did not change during reaction at 100 °C and 150 bar. The oxidation state of the Au particles was found to be metallic by XAS measurements (figure 3). No whiteline, which is typical for ionic gold, was observed in the X-ray absorption near edge spectra (XANES). This is in agreement with previous XPS measurements, which also demonstrated that gold was in the metallic state [36]. 1%Au/TiO_2(coll) showed a moderate activity resulting in a conversion of 16% at 99% selectivity to benzaldehyde, corresponding to a rate of 73 $\text{mol}_{\text{product}}\ \text{mol}_{\text{Au}}^{-1}\ \text{h}^{-1}$ and an estimated turnover frequency (TOF) of 161 h^{-1}. The turnover frequency was calculated considering the total number of surface Au atoms based on the mean particle size determined by STEM. 1%Au/Fe_2O_3(coll) was less active with a conversion of 10.4% (rate = 47 $\text{mol}_{\text{product}}\ \text{mol}_{\text{Au}}^{-1}\ \text{h}^{-1}$; TOF = 170 h^{-1}) and the 1%Au/C(coll) showed almost no activity; the conversion was only 2.4%. Au/C is known to be very active in the selective oxidation of diols and polyols [12,37–39]. For all three catalysts a very high selectivity of around 99% was obtained. Note that the respective catalytic system was not optimised. In all reactions with benzyl alcohol the only by-product found was benzyl benzoate, the amount of benzoic acid being below the detection limit of the gas chromatograph. To compare the use of carbon dioxide to solvent-free conditions the same experiments were carried out without CO_2. This solvent-free oxidation of benzyl alcohol on gold led to significantly lower conversions of 7% for 1%Au/TiO_2(coll) and 1%Au/Fe_2O_3(coll), and below 1% for 1%Au/C(coll). Since particles with a diameter between 1 and 4 nm were present in all three catalysts, the difference in activity cannot be solely explained by size effects. The different morphology of the gold particles on the different supports may be one of the reasons for the different catalytic activity [40–43], but also the support itself can contribute to the reaction, e.g. by interactions of the support with the solvent or reactants.

Since preparation routes and after-treatments are known to have a strong influence on catalytic behaviour [15,40,44], a calcined version (400 °C for 4 h) of the colloidal Au/TiO_2 catalyst was prepared. Furthermore, the same support was impregnated using $HAuCl_4$ and was tested as-prepared and calcined at 400 °C for 4 h. A 1%Au/Fe_2O_3 was made both by flame spray pyrolysis and by adsorption of gold colloids on the flame made support. The data are summarised in table 1. Whereas calcination led to a decrease of conversion from 16.0% to 10.4% for the colloidal Au/TiO_2 catalyst, it led to an increase from 0.9% to 1.7% for the corresponding impregnated catalyst. The very low values in the second case can be ascribed to the use of a chloride containing salt for the impregnation and the formation of large gold particles (up to 50 nm). For 1%Au/TiO_2(coll) an effect by calcination was clearly visible: sintering took place and the estimated mean particle size increased to 2.8 nm. Furthermore, the colloidal synthesis of Au/Fe_2O_3 led to better catalytic results than flame spray pyrolysis and resulted in smaller Au particles.

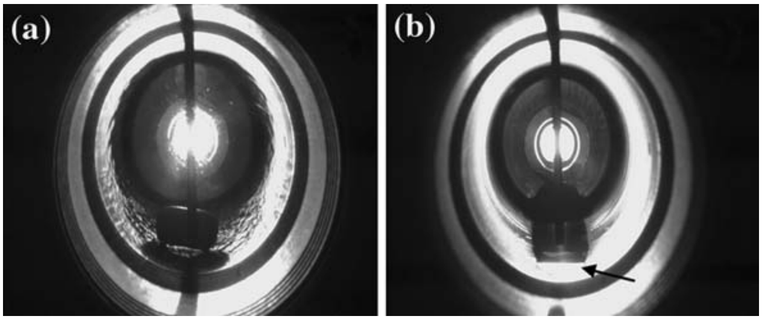

Figure 1. Snapshots of phase behaviour of the reaction mixture at 100 °C and 150 bar. Added amounts were (a) 0.4 mol% benzyl alcohol, 98.7 mol% CO_2, 0.9 mol% O_2 (single phase) and (b) the corresponding mixture with 6% O_2 (two phases; the arrow marks the CO_2-expanded liquid).

Table 1
BET surface areas, conversions and selectivities to benzaldehyde for different gold catalysts used for the selective oxidation of benzyl alcohol under single-phase conditions (100 °C and 150 bar for 3 h)

Catalyst	BET (m^2/g)	Conversion (%)	Selectivity to benzaldehyde (%)
1%Au/TiO_2(coll)	49	16.0	99.0
1%Au/TiO_2(coll) calcined[a]	48	10.4	99.1
1%Au/TiO_2(impregnated)		0.9	100[b]
1%Au/TiO_2(impregnated) calcined[a]		1.7	100[b]
1%Au/Fe_2O_3(coll)	189	10.4	99.0
1%Au/Fe_2O_3 by flame spray pyrolysis	219	5.5	100
1%Au/C(coll)	1311	2.4	99.1

Used amounts: 7 mmol benzyl alcohol, 14 mmol O_2, 1591 mmol CO_2.
[a] Calcination at 400 °C for 4 h.
[b] Amount of by-products below detection limit of the gas chromatograph.

As 1%Au/TiO_2(coll) showed the highest conversion at high selectivity, it was used as standard catalyst for the following studies. The dependence of the catalytic behaviour on different reaction parameters was investigated; table 2 shows the dependence on the reaction temperature. The conversion rose with increasing temperatures from 10% at 80 °C to 35% at 120 °C. Interestingly, the same trend was observed for the selectivity to benzaldehyde: 94% at 80 °C to > 99% at 120 °C.

In addition to the standard experiment using 1%Au/TiO_2(coll) with a reaction time of 3 h, longer time intervals of 6, 12 and 20 h were used (table 3). After 20 h a conversion of 30% was obtained. To check for a possible deactivation, the catalyst was recollected after a 3 h experiment and reused for another reaction. In this case only a conversion of 7% was observed after 3 h. In order to monitor the reaction in a time-resolved manner, the selective oxidation of benzyl alcohol was performed in a high-pressure view cell, equipped with IR transmission windows and an ATR-IR crystal on which 8 mg of the catalyst were coated. 2.3 mmol benzyl alcohol, 4.6 mmol O_2 and 523 mmol CO_2 were used resulting in a total pressure of 150 bar at 100 °C. As can be seen in figure 4 first an induction period of approximately 2 h occurred, similarly as in the oxidation of benzyl alcohol in $scCO_2$ over Pd/Al_2O_3 [45]. Then a linear increase of conversion followed and a slight deceleration occurred after ca. 15 h.

A change in the amount of oxygen and by that in the composition of the reaction mixture yielded a lower conversion for both less and more than 0.9 mol% (table 4); the amount of CO_2 was also changed to keep the pressure at 150 bar. Although an excess of oxygen is still available in the experiment with an O_2 molar concentration of 0.4% ($n(O)/n(\text{alcohol}) = 2$), the conversion dropped from 16% at 0.9 mol% O_2 to 12%. Increasing the initial oxygen pressure to 20 and 30 bar also lowered the conversion to 11.7% and 10.9%, respectively. The selectivity towards benzaldehyde ranged in all four cases between 97% and 99%.

To check the applicability of 1%Au/TiO_2(coll) in the high-pressure reaction system for different alcohols, 1-octanol and geraniol were chosen for oxidation under the same conditions as used for the oxidation of benzyl alcohol. 1-Octanol is known to be not very reactive in heterogeneously catalysed oxidations [11,16,46] and geraniol can yield various by-products, since it has several functional groups, that can be oxidised [23]. The conversion for 1-octanol was 4.1% at a selectivity of 90.4% towards octanal. The selective oxidation of geraniol yielded a conversion of 10.9% and a selectivity towards citral (combination of the two isomers geranial and neral) of 30.6%. The use of 1%Au/Fe_2O_3(coll) resulted in a higher conversion of 20.3% at similar selectivity. Note again that the system was not optimised for the highest possible performance.

Whereas hitherto experiments, except the ones at elevated oxygen pressure, were all conducted under single-phase conditions, the study of the reaction performance at different pressures, i.e. different amounts of added carbon dioxide, is accompanied in several cases by phase separations (cf. figure 1). This strongly affected the performance as reflected by the results in table 5. As already mentioned above, the conversion of the system 1%Au/TiO_2(coll)–O_2–alcohol without CO_2 was 7%. When 10 g of CO_2 were added, corresponding to a content of 91.6 mol% and a total pressure of 39 bar at 100 °C, the conversion increased to 22.4%, whereas the selectivity remained almost unchanged (95.2% vs. 96.4% upon CO_2 addition). Addition of 30 g CO_2 (97.0 mol%, 90 bar) resulted in an equally high conversion of 23.6% and a selectivity of 97.0%. When 70 g (150 bar) and 90 g (177 bar) of carbon dioxide were used (98.7 mol% and 99.0 mol%), the conversion decreased to 16.0% and 16.3%, respectively, whereas the selectivity to benzaldehyde increased to 99% and >99%.

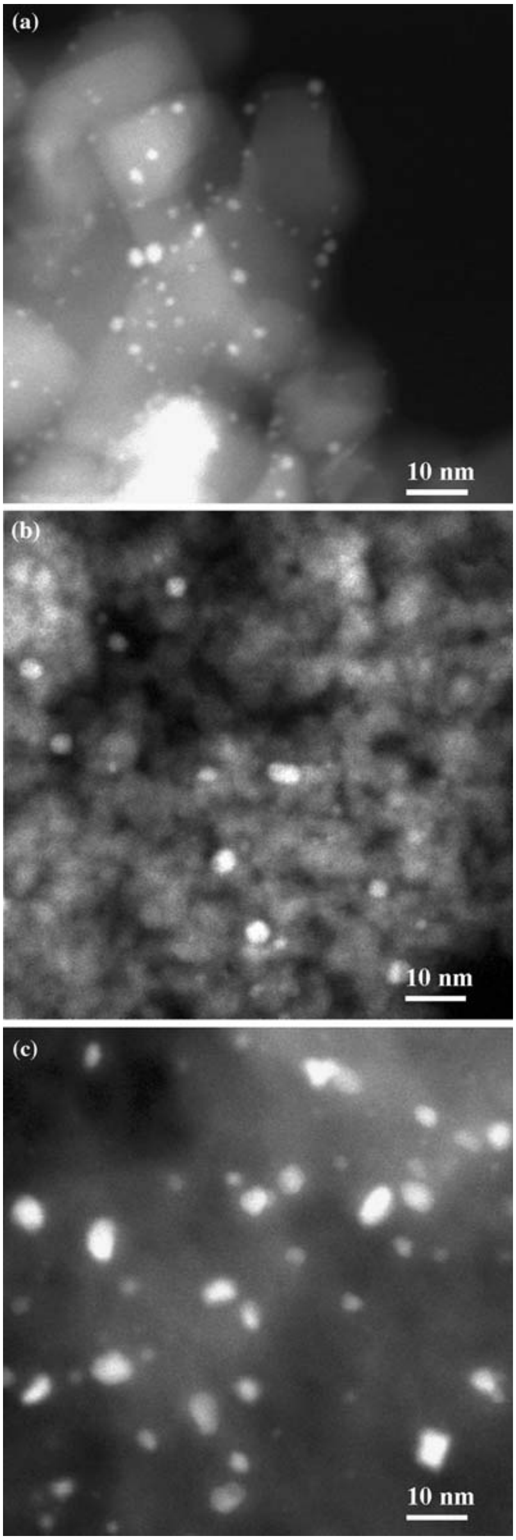

Figure 2. HAADF-STEM images of (a) 1%Au/TiO_2(coll), (b) 1%Au/Fe_2O_3(coll) and (c) 1%Au/C(coll). The gold particles appear as bright spots on the respective support (confirmed by EDX).

4. Discussion

Our studies demonstrate that supercritical carbon dioxide has a beneficial effect on the reaction rate of the gold catalysed selective oxidation of benzyl alcohol. Conversions of 16.0% and 10.4% (TOF: 161 h^{-1} and 170 h^{-1}) for 1%Au/TiO_2(coll) and 1%Au/Fe_2O_3(coll), respectively, under single-phase conditions were higher than those achieved in the reference experiment without CO_2 and solvent-free oxidation reactions reported in literature [11,13]. The selectivities were higher than for other noble metals like platinum or palladium [7,22], and in several cases close to 100%. Using scCO_2 as solvent, aerobic alcohol oxidation with molecular oxygen as sole oxidant could be performed and the addition of an assisting base circumvented. However, base-catalysed oxidations typically showed higher reaction rates, particularly in the beginning of the reaction [12,47]. Despite the fact that carbon dioxide has a beneficial effect on the reaction rate, single-phase conditions were not the most optimal ones. Table 5 shows, that the rate is highest under conditions where a CO_2-expanded reactant phase is present. A similar behaviour has also been observed in other studies [24,48]. This observation as well as the fact that 1%Au/TiO_2(coll) and 1%Au/Fe_2O_3(coll) show the same activity in the absence of CO_2, but a different one in its presence, indicate that carbon dioxide may affect the properties of the catalytic liquid/solid interface, either by enhanced molecular mass transfer or chemical interaction with the support material. Depending on the hydrophilicity/hydrophobicity of the support this interaction will be weaker or stronger causing differences in sorption behaviour and basicity [20,21].

Calcination of 1%Au/TiO_2(coll) at 400 °C for 4 h caused sintering of the gold particles. The estimated mean particle size increased from 1.9 to 2.8 nm, and a conversion drop to 10.4% was observed. Fl-XANES spectra showed that the gold was in the reduced (metallic) state before as well as after the reaction (figure 3).

The increase of activity with reaction temperature (see table 2) has been expected. But, a simultaneous increase of the selectivity to benzaldehyde was observed. An explanation could be the higher diffusivity of the reactant in the catalyst particle in the supercritical system at higher temperatures, which would allow faster diffusion of the aldehyde into the bulk phase and thus a lower probability for further reaction [21].

The decrease of reaction rate, indicated by reactions of different durations in the autoclave and the experiment in the high-pressure view cell, that was monitored by IR spectroscopy is not yet completely understood. The effect cannot be solely explained by deactivation of the catalyst, since the recycled catalyst still exhibited a certain conversion. Also no indication for changes of the gold particle size or leaching of gold was found. For example, HAADF-STEM pictures of 1%Au/TiO_2(coll) before and after reaction at 100 °C and 150 bar for 3 h did not show any significant difference and by atomic absorption spectroscopy no gold could be detected in the filtered solution after reaction. A possible explanation

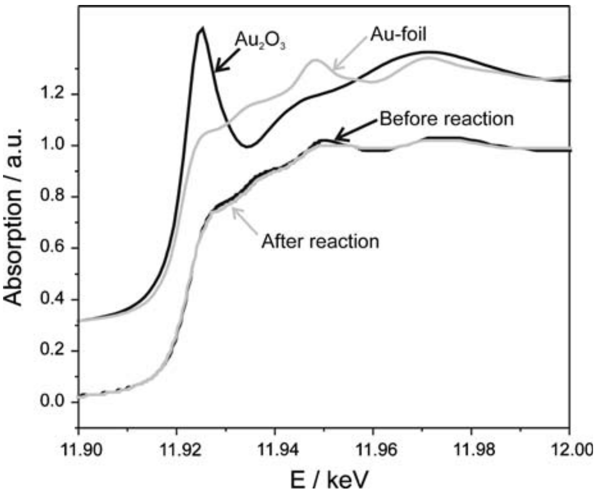

Figure 3. XANES spectra taken in fluorescence mode of 1%Au/TiO_2(coll) around the Au L_3-edge between 11.90 and 12.00 keV before (black line) and after reaction (grey line); for comparison the spectra of Au-foil and Au_2O_3 are given above.

is the influence of water, which, although in certain cases beneficial for CO oxidations [49,50], is detrimental for alcohol oxidations because of its low solubility in the non-polar solvent CO_2 [45,51]. Experiments showed that after the addition of small amounts of water (0.2–0.8 mol%) the conversion decreased by up to 60% (table 3). This observation could be traced to different reasons such as blocking of active sites or changes of surface properties.

Table 2
Conversions, selectivities and reaction pressures of the oxidation of benzyl alcohol to benzaldehyde on 1%Au/TiO_2(coll) at different reaction temperatures after 3 h (7 mmol of alcohol, 14 mmol oxygen and 1591 mmol CO_2)

Reaction temperature (K)	Reaction pressure (bar)	Conversion (%)	Selectivity to benzaldehyde (%)
353	133	9.6	93.6
373	150	16.0	99.0
393	167	34.7	99.2

Table 3
Conversions and selectivities to benzaldehyde for the selective oxidation of benzyl alcohol on 1%Au/TiO_2(coll) under single-phase conditions (100 °C and 150 bar) for different reaction times. Used amounts: 7 mmol benzyl alcohol, 14 mmol O_2, 1591 mmol CO_2

Reaction time (h)	Conversion (%)	Selectivity to benzaldehyde (%)
3	16.0	99.0
6	16.9	99.0
12	24.1	> 99.0
20	30.1	> 99.0
3[a]	9.1	98.3

[a] Addition of 11 mmol of H_2O before the reaction.

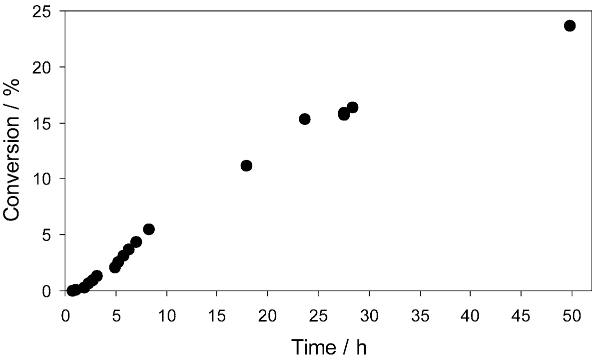

Figure 4. Monitoring of the selective oxidation of benzyl alcohol to benzaldehyde in a high-pressure view cell by IR transmission spectroscopy; plot of alcohol conversion over reaction time in hours. Used amounts were 2.3 mmol benzyl alcohol, 4.6 mmol O_2 and 523 mmol CO_2 at 150 bar and 100 °C. The ATR-IR crystal was coated with 8 mg of 1%Au/TiO_2(coll).

The influence of the added amount of oxygen presents itself in two ways: A lower amount than 0.9% leads to lower conversion, possibly because its concentration at the solid–liquid interface is too low. A higher amount of oxygen also leads to lower conversions, which may be explained by the formation of a two phase system, which reduces mass transfer [22].

Finally, although the best results were achieved for the model compound benzyl alcohol, extension of the combined application of gold-based catalysts and supercritical CO_2 seems also interesting for other alcohols, as our preliminary experiments with 1-octanol and geraniol show. Conversions of 4.1% and 20.3%, respectively, and selectivities of 90.7% and 30.6% can probably be improved by further optimisation.

5. Conclusions and outlook

We could show that the environmentally friendly selective oxidation of benzyl alcohol over supported gold catalysts in supercritical CO_2 both under single-phase and two-phase conditions yielded a higher conversion than the same reaction without any solvent. Especially the selectivity, with values very close to 100% underscored the advantageous properties of both gold as catalytic material and dense carbon dioxide as a reaction medium. Furthermore, this reaction was proven to take place with only molecular oxygen as oxidant without requiring the presence of an auxiliary base. The catalytic activity depends on various parameters such as type of support, kind of preparation method, and size and probably morphology of the gold particles. Gold catalysis combined with the application of dense carbon dioxide offers interesting opportunities for aerobic oxidation of probably a variety of substrates, including several other alcohols, as shown here for 1-octanol and geraniol. However, further investigations are needed to gain deeper insight into the functioning of these catalytic

Table 4
Conversions and selectivities to benzaldehyde for different molar ratios of oxygen in the selective oxidation of benzyl alcohol on 1%Au/TiO_2(coll)

Amount of oxygen (mmol)	Molar ratio of oxygen (%)	Amount of CO_2 (mol)	Conversion (%)	Selectivity to benzaldehyde (%)
7	0.4	1.61	12.0	98.2
14	0.9	1.59	16.0	99.0
81	6.0	1.27	11.7	98.6
122	10.6	1.02	10.9	97.4

The amount of alcohol was kept constant at 7 mmol, the amount of CO_2 was adjusted to maintain a reaction pressure of 150 bar.

Table 5
Conversion, selectivity to benzaldehyde and reaction pressure for different molar ratios of carbon dioxide in the selective oxidation of benzyl alcohol on 1%Au/TiO_2(coll)

Amount of CO_2 (mol)	Amount of CO_2 (g)	Reaction pressure (bar)	Conversion (%)	Selectivity to benzaldehyde (%)
0	0	3.4	7.0	95.2
0.23	10	38	22.4	96.4
0.68	30	90	23.6	97.0
1.59	70	150	16.0	99.0
2.05	90	177	16.3	98.0

The amounts of alcohol and oxygen were kept constant at 7 and 14 mmol, respectively.

systems using *in situ* spectroscopic methods and structurally tailored catalysts.

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