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Promoting effect of water for aliphatic primary and secondary alcohol oxidation over platinum catalysts in dioxane/aqueous solution media

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ABSTRACT

In the selective oxidation with air of 1-octanol and 2-octanol in 1,4-dioxane at 100 °C and 10 bar in the presence of carbon supported platinum catalysts, the catalytic activity could be impressively boosted by substitution of pure dioxane by increasing amounts of water. Changing the polarity of the solvent strongly influences the adsorption equilibrium of substrates and products at the catalyst surface and hence plays an influential role on the reaction rate.

1. Introduction

Liquid phase oxidation of alcohols is an important transformation since the corresponding aldehyde, ketone or carboxylic derivatives serve as important and versatile intermediates for the synthesis of fine and specialty chemicals [1–3]. For environmental and economic significance, use of molecular oxygen as a green, efficient and selective oxidant has received growing attention; water is then the only by-product of the process. Accordingly, many homogeneous [3–9] and heterogeneous [10–41] catalyzed selective oxidations of alcohols, using molecular oxygen as oxidant, have been reported. Because of their facile handling, separation and recycling, solid catalysts, in particular a wide range of supported and/or immobilized noble metals [for reviews, see 14,39–41,49] attracted much attention. Various supported platinum [15,16,19–21], palladium [22–24], ruthenium [13,25–28], gold [29–37], Pd–Au [36,37] or Pt–Au [42,43] catalysts have been proposed, in some cases with modifier (such as Bi) [44,45]. Also, differently stabilized soluble metal nanoparticles are in development as efficient catalysts in water [29,50–54] or aqueous/organic media [55].

In the class of alcohols surveyed, non-activated aliphatic alcohols are usually much more demanding substrates for this kind of reaction compared with aromatic or allylic alcohols [15,25,46–48,51–54,56–58]. The following few examples illustrate the poor reactivity of such alcohols. Microgel-stabilized soluble Pd nanoclusters (1 mol.%) were able to oxidize 1-phenylethanol to completion in water at 100 °C after 6 h, but 2-octanone yield from 2-octanol under the same conditions was only 7% after 24 h [51]. Over a silver-based catalyst, different alcohols could be converted with high conversion and selectivity at room temperature under molecular oxygen atmosphere while 2-octanol afforded only moderate yields of 2-octanone [56]. In the presence of polymer-incarcerated, carbon-stabilized gold nanoclusters (1 mol.%), whereas several aromatic and allylic alcohols were oxidized smoothly to afford the corresponding ketones in quantitative yields, secondary aliphatic alcohols were less reactive [57]. A Ru/MnO_x/CeO_2 catalyst showed high activity at room temperature and atmospheric O_2 for the oxidation of different alcohols in trifluorotoluene, and 2-octanol was oxidized to 2-octanone in 83% yield. However, longer reaction time than other activated benzylic and allylic alcohols were required [58]. Uozumi et al. [52,53] prepared amphiphilic polystyrene-polyethylene glycol (PS-PEG) resin-supported nanoparticles of palladium and platinum which catalyzed oxidation of alcohols in refluxing water at 100 °C with atmospheric pressure of molecular oxygen. In the presence of Pd (1 mol.%), secondary α-arylated alcohols, such as 1-phenylethanol, diphenylmethanol, 1-hydroxyindane gave acetophenone, benzophenone, and indanone in 99, 85, and 95% yield, respectively. In contrast, oxidation of alicyclic and aliphatic alcohols was inadequate [52]. On the other hand, using the Pt nanocatalyst, 2-, 3- and 4-octanol were efficiently converted to the corresponding ketones in 81–93% yield [53]. This is also the case if Pt nanoclusters synthesized via reduction by glycol and stabilization by PV are used. They showed high efficiency to oxidize 2-octanol in water at 80 °C

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under 1 bar O_2 with a 94.2% yield of 2-octanone after 24 h and were stable [54]. Pd nanoparticles encapsulated in a hollow porous carbon sphere or Pd supported catalysts did not show any catalytic activity for oxidation of 1-octanol in K_2CO_3 aqueous solution at 80 °C, while excellent catalytic activity was observed for oxidation of various primary benzylic or allylic alcohols [59].

As concerns the solvent, water is the preferred one. It has been widely used for water-soluble substrates, in particular for carbohydrates [36,37]. However, most alcohols, among them octyl alcohols, are poorly soluble in water even at high temperatures or very few catalysts are active for a wide range of alcohols in water. Therefore, many experiments in the literature for hydrophobic substrates were achieved in the presence of organic flammable solvents (toluene, xylene, trifluorotoluene, acetonitrile, cyclohexane...) which ensure dissolution of the substrate [15,23,60]. Excellent properties of various catalysts were shown. The experiments in organic solvents are usually performed at lab-scale in very small volumes of reactor (typically only a few mL solvent). However, despite these progresses, there are still serious safety issues associated with the use of dioxygen with these oxidisable organic solvents [61]. A solution proposed to overcome the low water solubility was the use of an amphiphilic insoluble polymer support to achieve a local favourable environment for adsorption of the alcohol [52,53]. Supercritical CO_2 has also been proposed as an alternative solvent [62–66]. Thus, over Pd/Al_2O_3, 2-octanol (5 mol.%) was oxidized to 2-octanone in almost 100% selectivity at 120 °C under 95 bar total pressure and a contact time of 1.02 g h mol^{-1} in a continuous reactor. However, conversions were moderate because of the difficulties to dissipate the heat produced by the exothermic reaction [62]. Also, in a miniature reactor, 75% yield of 2-octanone was achieved with *a* > 90% mass balance over a 5 wt.%Pt–1 wt.%Bi/Al_2O_3 catalyst [66].

The nature of the solvent on the performances of the catalyst for alcohol oxidation may be important and has scarcely been studied. With a Ru/C catalyst (5 mol.%) at 50 °C under atmospheric molecular oxygen, 1-phenyl-1-pentanol was for instance efficiently oxidized in toluene to valerophenone (93% conversion after 24 h), whereas the conversion was moderate in acetonitrile (57% conversion) and very low in t-BuOH or DMSO (13 and 4%, respectively) [67]. High throughput screening of platinum group metal catalysts for the selective oxidation of several alcohols under mild conditions (<70 °C and <5 bar) concluded that toluene and xylene were the most effective solvents [15]. In the oxidation of 2-octanol with a Pt–Bi/C catalyst, the reaction rate was very dependent on the composition of dioxane/heptane mixtures [68]. It was also demonstrated that water may play an influential role. The catalytic activity in the oxidation of benzylalcohol in xylene over Au/TiO_2 [69] or in toluene over carbon nanotube-supported Ru catalysts [70] could be significantly promoted by water. In these multiphase reaction systems, the solid catalyst formed emulsion droplets at the interface of the two liquid phases.

Dioxane is very hydrophilic and a water-miscible organic solvent largely used in oxidation reactions in the fine chemicals and pharmaceuticals industry. We previously reported on the use of dioxane as solvent for the oxidation of benzyl alcohol derivatives using Pt/C catalysts [20,21]. By changing the solvent from dioxane to dioxane/alkaline aqueous solution mixtures, it was possible to tune the selectivity of benzylalcohol derivatives to the aldehyde or to the carboxylic acid. Under the conditions used (<100 °C, <10 bar air), this solvent did not undergo oxidations and no solvent-derived by-products were observed. The reaction rate of oxidation of the alcohol was also greatly enhanced. In line with our previous work [20,21] we now present the catalytic oxidation of 1-octanol and 2-octanol selected as model substrates for aliphatic alcohols in dioxane and dioxane/water solvent with the aim to improve the potential of classical platinum supported on activated carbon catalysts.

2. Experimental

2.1. Catalyst preparation

The supported metallic catalysts were prepared on a synthetic carbon from MAST Carbon Technology Ltd. The mesoporous carbon was prepared by carbonisation at 800 °C of a porous polymeric resin prepared from a phenolic resin and hexamethylenetetramine in ethyleneglycol and activation using CO_2 at 850 °C. The catalysts were prepared by impregnation of the carbon with an aqueous solution of hexachloroplatinic acid followed by liquid phase formaldehyde reduction [20,21]. The aqueous solutions of the precursors used for the preparation were in the appropriate concentrations to obtain Pt loadings of 3–5 wt.%. The Pt–Bi catalysts were prepared by redox surface reaction from an aqueous $BiONO_3$ glucose solution, according to previously reported procedure [11]. By this way, Bi is directly and preferentially deposited on the noble metal.

2.2. Characterization of materials

The surface area and pore volume of the carbon were determined from analyses of nitrogen gas adsorption isotherms at −196 °C performed with a Micromeritics ASAP 2020. The sample was degassed at 350 °C for 3 h prior to analysis. X-ray diffraction characterizations were performed using a Siemens D5005 diffractometer with CuKα radiation at 0.154184 nm. Transmission electron microscopy (TEM) direct observations of the catalysts were conducted using a JEOL 2010 microscope (200 kV, resolution 0.19 nm).

2.3. Catalyst evaluation in the aerobic oxidation of alcohols

The reaction tests were performed under a set of realistic conditions in a stirred autoclave reactor of 300 mL made of Hastelloy in batch mode equipped with a magnetically driven stirrer set. In a typical oxidation reaction, the reactor was loaded with a mixture of alcohol (15 mmol) and solvent (150 mL) and the supported catalyst, to get a 1 mol.% Pt with respect to the alcohol. After purging with argon, the reactor was heated to the desired reaction temperature, and then air was introduced up to the pressure of 10 bar. Efficient stirring was started and this time was considered to be zero time for the reaction.

Liquid samples were periodically withdrawn from the reactor and analysed along the reaction course. The quantitative analysis of the reactants and products was carried out by Gas Chromatography (GC) equipped with a Flame Ionisation Detector (FID) and a DBWax column (30 m × 0.25 mm, 0.25 μm film thickness) using acetophenone as external standard. In the case of high amounts of water in dioxane which do not ensure good solubility of the substrate and the products, only the final solution was analysed; at the end of the reaction, dioxane was added to the reaction medium, the catalyst was filtered off and the sample was analysed. Recoveries were always very good with this procedure. In some experiments, the isolated yield was calculated. After the given reaction time, the reaction solution was transferred into a separation funnel, diluted with water (25 mL), and extracted with an equal volume of EtOAc (3 aliquots of 25 mL). The organic layer was analysed by ^{1}H NMR to determine the content in reactant and products.

^{1}H NMR data were conform to the literature:

2-Octanol (^{1}H NMR, 250 MHz, $CDCl_3$): δ 3.80 (m, 1 H); δ 1.83 (s, 1 H); δ 1.40 (m, 10 H); δ 1.18 (d, 3 H, J_{ab} = 6.1 Hz); δ 0.86 (t, 3 H, J_{ab} = 6.2 Hz).

2-Octanone (^{1}H NMR, 250 MHz, $CDCl_3$): δ 2.40 (t, 2 H, J_{ab} = 6.8 Hz); δ 2.13 (s, 3 H); δ 1.57 (m, 2 H); δ 1.30 (m, 6 H); δ 0.86 (t, 3 H, J_{ab} = 6.7 Hz).
1-Octanol (^{1}H NMR, 250 MHz, $CDCl_3$): δ 3.61 (t, 2 H, J_{ab} = 6.7 Hz); δ 1.77 (s, 1 H); δ 1.60 (m, 2 H); δ 1.26 (m, 10 H); δ 0.86 (t, 3 H, J_{ab} = 6.5 Hz).
Octanal (^{1}H NMR, 250 MHz, $CDCl_3$): δ 9.76 (t, 1 H, J_1 = 2.1 Hz); δ 2.42 (td, 2 H, J_1 = 2.1 Hz, J_2 = 6.7 Hz); δ 1.63 (m, 2 H); δ 1.30 (m, 8 H); δ 0.87 (t, 3 H, J_2 = 6.7 Hz).
Octanoic acid (^{1}H NMR, 250 MHz, $CDCl_3$): δ 11.6 (s, 1 H); δ 2.34 (t, 2 H, J_{ab} = 6.7 Hz); δ 1.63 (m, 2 H); δ 1.29 (m, 8 H); δ 0.88 (t, 3 H, J_{ab} = 6.7 Hz).

The platinum contents in the reaction medium were checked by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of the filtrates at the end of the reactions. All measures were below the detection limit (<0.1 ppm), showing no leaching of the catalyst. Similarly, when Bi promoted catalysts were used, no leaching of this metal was detected.

3. Results and discussion

3.1. Characterization of the platinum catalysts

The specific surface area of the support was 1265 $m^2\,g^{-1}$ with average pore sizes of 3.4 and 11 nm.

Several batches of Pt catalysts with different loadings in the range of 2.5–4.7 wt.% were prepared during this study. XRD of all the solids demonstrated that no diffraction peak characteristic of the Pt phase could be observed, indicating that the Pt crystallites were probably well dispersed. Fig. 1 shows typical TEM images of a 2.8%Pt/C. The sample consisted of relatively small Pt particles homogeneously distributed throughout the carbon surface with a metal particle size around 2 nm. Some aggregates of these small particles were also observed.

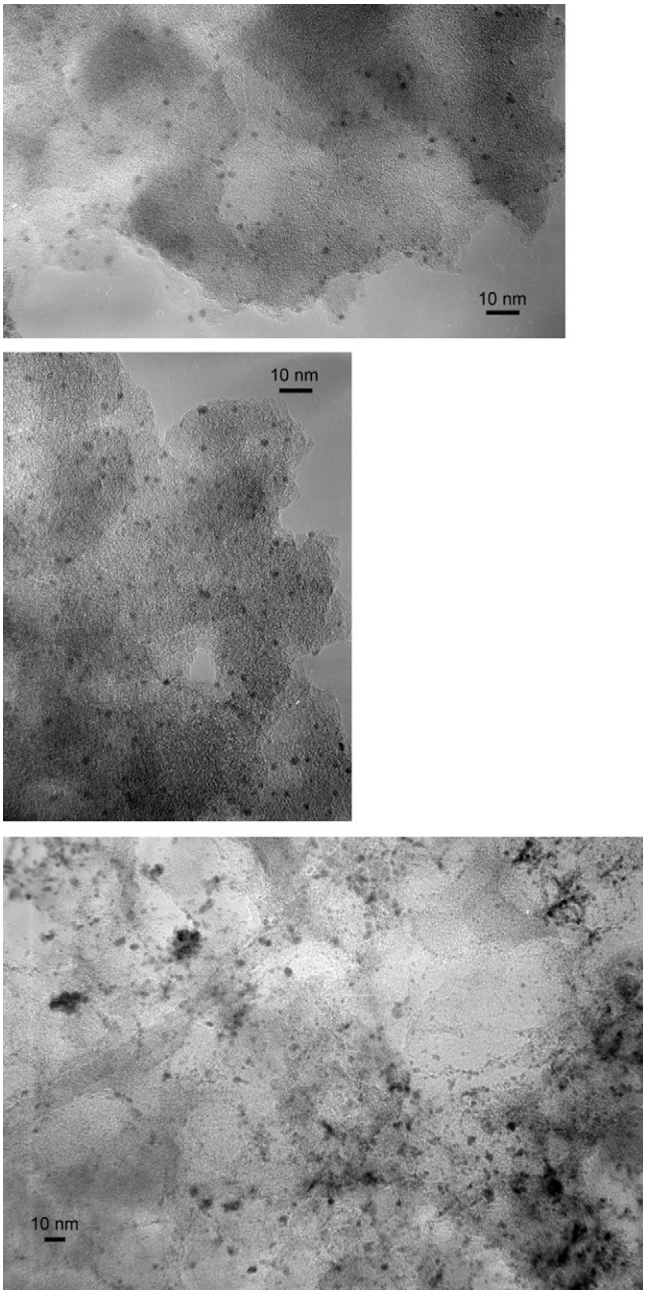


Fig. 1. TEM representative images of 2.8%Pt/C catalyst.

3.2. Influence of the solvent in the oxidation of 1-octanol and 2-octanol in the presence of Pt/C catalyst

The catalytic activity of the Pt catalysts was investigated in the oxidation of 1-octanol at 100 °C and 10 bar air. The tests were conducted with a substrate/metal ratio of ca. 100. Fig. 2 shows the concentrations vs. reaction time profiles for experiments in dioxane (a), in dioxane/water 90%/10% (b) and 50%/50% (c), using a Pt/C catalyst. 1-octanal and 1-octanoic acid were the sole products under the present reaction conditions. It was observed that no significant conversion occurred during heating under inert atmosphere (time < 0).

The results clearly show that catalyst activity is strongly dependent on the nature of the solvent.

In dioxane (Fig. 2a), the catalyst was very active initially and the conversion reached 36% within one hour. Then, the reaction rate slowed down progressively and the conversion stopped at ca. 60% after 6–8 h of reaction, indicating severe deactivation of the catalyst. Under these conditions, both the aldehyde and the acid were formed from the beginning of the reaction, and the final selectivity was slightly in favour of the aldehyde (54%). Previously, we have shown that the use of dioxane as solvent for substituted benzylalcohol afforded the aldehyde very selectively with complete conversion [21,22]. This tendency toward further oxidation of the aldehyde was expected, because of the easier hydration of the aliphatic aldehyde and formation of the gem-diol compared to an aromatic aldehyde. Water formed in the reaction can react with the aldehyde to form very easily an aldehyde hydrate, which further reacts to give acid. Indeed, when high selectivity to the aldehydes is expected, screening of the literature suggests that Ru-based catalysts would be a better option [15,45].

When dioxane/water 90%/10% and 50%/50% (v/v) were employed as the solvent, the initial reaction rate of oxidation of 1-octanol was clearly greatly enhanced (Fig. 2b and c). Conversion after one hour was 73% and 67%, respectively, compared to 36% in pure dioxane. However, a severe deactivation was also observed and 1-octanol conversion was rapidly limited to ca. 70%. The selectivity of each oxidation reaction was also determined. We noted that while the major product in dioxane was 1-octanal, the major product was 1-octanoic acid in both dioxane/aqueous solutions. The selectivity to octanoic acid shifted from 46% in dioxane to 69% in dioxane/water 50%/50% in the final solutions. Water can react with the aldehyde to form the aldehyde hydrate, which further reacts to form 1-octanoic acid. Note that octyloctanoate was never detected and that no total selectivity toward the aldehyde was obtained at that point of the study.

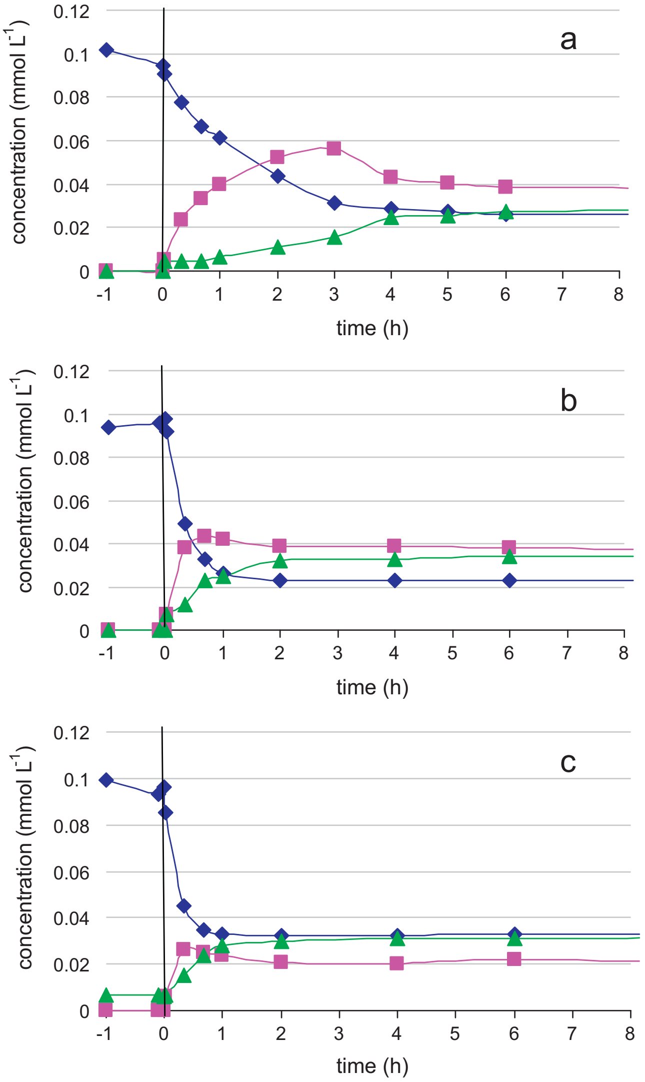


Fig. 2. Oxidation of 1-octanol in dioxane (a), dioxane/water 90%/10% (b) and 50%/50% (c) in the presence of 2.9%Pt/C (a) or 4.7%Pt/C (b and c). Reaction conditions: 150 mL 0.1 mol L^{-1} 1-octanol, 100 °C, 10 bar air, 1-octanol/Pt molar ratio = 100, (◆) 1-octanol, (■) 1-octanal, (▲) 1-octanoic acid.

Similarly, the oxidation of 2-octanol to 2-octanone was carried out in dioxane and in dioxane/water mixtures. The effect of water on the catalytic activity of the platinum catalyst is shown in Fig. 3.

It appears from these data that addition of water to dioxane also plays a key role in the oxidation rate of 2-octanol. In dioxane, the Pt/C catalyst showed low activity and it afforded a conversion of only 29% within 6 h. When a dioxane/water 66%/34% mixture was used, a 60% conversion was achieved. A further increase in the water concentrations to 50 vol.% led to a jump to 100% after only 1 h reaction. In all these experiments, the reaction gave rise to the formation of 2-octanone in quantitative yields. No other products beside 2-octanol, 2-octanone and the internal standard could be detected by GC. The purity of the product was checked by ^{1}H NMR analysis.

The reaction profiles in dioxane or dioxane/water mixtures for 2-octanol are slightly different from the one described by Mounzer et al. [68]. Upon oxidation of 2-octanol in heptane or xylene (0.248 M, 3 g of 5%Pt–1%Bi/C, 70 °C, atmospheric pressure), the reaction rate decreased dramatically shortly after the start of the reaction.

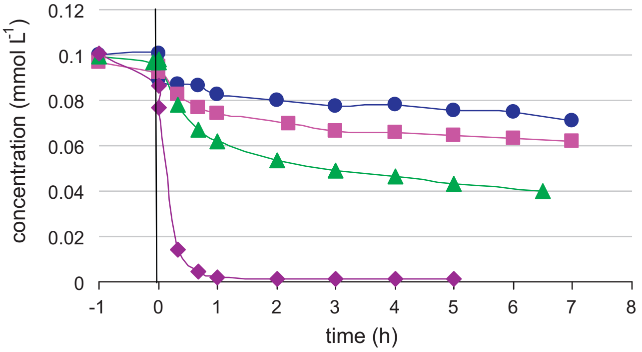


Fig. 3. Promotion effect of water on the catalytic oxidation of 2-octanol to 2-octanone in dioxane/water mixtures in the presence of 2.8%Pt/C. Reaction conditions: 2-octanol (0.1 mol L^{-1}), Pt/C (1 mol.% Pt), solvent (150 mL), 100 °C, 10 bar, (●) dioxane, (■) dioxane/water 75%/25%, (▲) dioxane/water 66%/34%, (◆) dioxane/water 50%/50%.

An experiment was also performed, using a dioxane/water 25%/75% ratio. However, under these conditions, total solubility of 2-octanol was not obtained and the reaction was performed in biphasic conditions without following the concentration profiles. After 1 h, after cooling and depressurization, dioxane was added to the reaction medium to obtain complete solubilization. Analysis of the final solution demonstrated total conversion of 2-octanol and total selectivity to the ketone, which suggests that oxidation can be carried out even if the reactant is not totally soluble. The higher the water content, the higher the activity.

To deeper understand the possible role of water on the catalytic activity and the deactivation of the catalyst, another set of experiments was performed at the lower temperature of 60 °C. The effect of substitution of a fraction of dioxane with water and the influence of sodium hydroxide addition was also examined.

The results for 1-octanol are illustrated in Fig. 4. As expected a decrease of the reaction temperature leads to a strong decrease in catalyst activity, but the reaction could go up to complete conversion. In dioxane/water 50%/50% with addition of 0.03 equiv. base, although a reaction time of 25 h was needed at that temperature, conversion was total with a complete selectivity to the carboxylic acid. However, a significant lower activity was obtained with the addition of a too large amount of NaOH (0.5 equiv.). As observed at 100 °C, the replacement of some dioxane by water progressively shifted the selectivity from the aldehyde to the acid. After 1 h, the selectivity to the aldehyde was 90%, 68%, 54% and 6%, in dioxane, dioxane/water 50%/50% or dioxane/alkaline aqueous solutions,

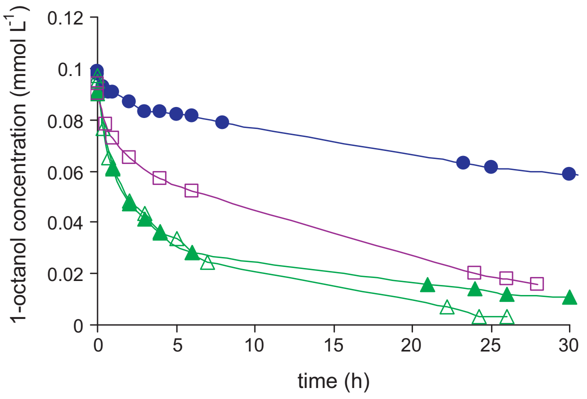


Fig. 4. Oxidation of 1-octanol in dioxane/water solvent in the presence of Pt/C at 60 °C. Reaction conditions: 1-octanol 0.1 mol L^{-1}, Pt 1 mol.%, 150 mL solvent, 10 bar, (●) dioxane, (▲) dioxane/water 50%/50%, (△) dioxane/water 50%/50% and 0.03eq. NaOH, (□) dioxane/water 50%/50% and 0.5 eq. NaOH.

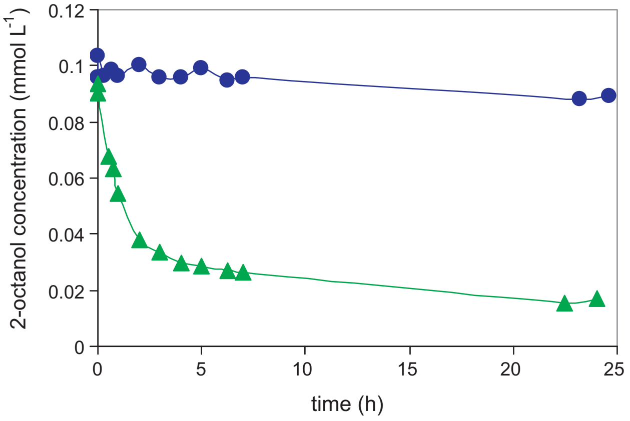


Fig. 5. Oxidation of 2-octanol in dioxane (●) and dioxane/water 50%/50% (▲) solvent in the presence of 2.8%Pt/C at 60 °C. Reaction conditions: 2-octanol 0.1 mol L^{-1}, Pt 1 mol.%, 150 mL solvent, 10 bar.

respectively. At the end of the reactions, selectivity to the aldehyde was 88% in dioxane while it was nearly total to the acid in the aqueous solvents. These results also confirm that the acid formed, even with high selectivity, does not poison the catalyst, under these reaction conditions.

Similarly, 2-octanol was oxidized in the presence of 2.8%Pt/C at 60 °C (Fig. 5). In the absence of water, the conversion of 2-octanol was less than 12% after 24 h, whereas in the dioxane/water 50%/50% solvent, conversion reached 85% at that time. Again, a much higher activity was observed in the dioxane/water system.

Considering the results obtained with 1- and 2-octanol, we tentatively examined the possible reasons why the combination of dioxane and water led to a substantial increase in activity, and why deactivation of the platinum catalyst was sometimes observed. We evaluated a range of parameters on the conversion of these alcohols to deeper understand the mechanism.

3.3. *Nature of catalyst deactivation*

According to the most accepted model, the actual mechanism of such heterogeneous oxidation is an oxidative dehydrogenation mechanism, in which the substrates are adsorbed and dehydrogenated on the metal surfaces. The adsorbed hydrogen atoms react with oxygen to form water [17] (Scheme 1).

However, deactivation is a problem which is often encountered in this type of oxidation over Pd or Pt nanoparticles and remains a challenge. Various processes for deactivation have been mentioned [44,45]: overoxidation (oxygen poisoning), sintering of metal particles, metal leaching, blocking of active sites by strongly adsorbed reactant, products or degradation by-products. We examined the different possible causes.

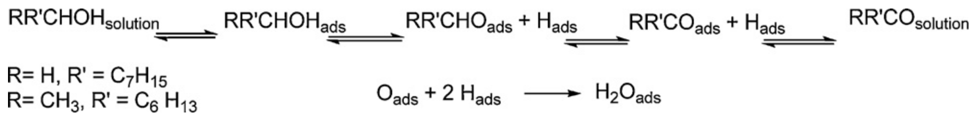
The possibility that deactivation was due to metal leaching or sintering in the present conditions was disregarded. As mentioned in the experimental part, analysis of the final solutions showed no observable loss of metal. Also, XRD observations of the used catalysts did not detect Pt diffraction peak, as in the fresh catalyst.

We supposed that during oxidation of 1-octanol, deactivation could be due to the production of 1-octanoic acid which strongly adsorbs on the catalytic sites, lowering their availability for alcohol oxidation. Further experiments were performed using the dioxane/water 50%/50% solvent and adding two different quantities of NaOH (0.03 equiv. or 0.5 equiv. based on 1-octanol initial concentration). The conversion profiles of 1-octanol were not significantly modified (Fig. 4). The selectivity to the acid was still higher (>90%), since the hydration of the aldehyde is favoured under basic conditions.

Another source of deactivation is decarbonylation of the carbonyl formed upon alcohol oxidation, affording adsorbed CO and a hydrocarbon residue. Adsorbed CO or hydrocarbon residues are likely responsible for site blocking and deactivation. Many studies have demonstrated this possible decarbonylation over Pd or Pt, either using model catalysts [71,72] or real powder catalysts [73]. Applying attenuated total reflection (ATR) spectroscopy, information could be obtained on the species adsorbed to the catalyst surface. It was revealed that CO was present on the surface in the absence of oxygen, though it was not observed under air over Pt/Al_2O_3 [41]. In our experiments, consistent with the observation that the ketones are more resistant to decarbonylation than are aldehydes [72], lower deactivations were observed in the oxidation of the secondary alcohol, 2-octanol (compare Figs. 2 and 3). On the other hand, no formation of hydrocarbons could be detected in solution by GC analysis during 1-octanol or 2-octanol reaction, which suggests that decarbonylation does not occur during this reaction, unless the carbonaceous residues remained adsorbed.

Deactivation of Pt catalysts by overoxidation of the particle surface, i.e. oxygen atoms penetration into the most external layers of metal crystals thus forming “subsurface” oxygen is often mentioned [44,45]. Alcohol oxidation has been shown to be regularly faster under mass-transport limiting conditions. Oxygen dissolved from the gas phase should be just present to react with hydrogen present at the surface but not to oxidize the metal surface. Oxygen solubility changes with the composition of the solvent. In particular, it is known that the oxygen solubility is much lower in water than in dioxane and other organic solvents [74]. Hence, the amount of oxygen should be lower in water-containing dioxane. If overoxidation was due to an excess dissolved oxygen concentration in pure dioxane, the catalyst should be less deactivated as far as water is added to the reaction medium and decreasing the solubility of oxygen. Indeed, this is what was observed upon replacing dioxane with water, which suggests that some mass transport limitation was then generated for the reaction.

To further understand the reason of deactivation during oxidation of 1-octanol, a supplementary experiment was performed in dioxane/water 50%/50%. After 5 h, when the conversion attained a plateau at 64% conversion, the reactor was cooled to room temperature and depressurized. After flushing under argon at room temperature, the reaction medium was again heated to the reaction temperature of 100 °C and pressurized to 10 bar. The reaction immediately started again. However, after 2 h more reaction, conversion reached a new plateau at 93%. Similarly, when 1-octanol was added in the reaction medium after cooling and purging with argon and before re-heating and adding air pressure, the catalyst was able to oxidize half of the 1-octanol before new deactivation. Typically, these results show that the supported platinum catalysts may suffer from deactivation caused by reversible overoxidation of active sites. The above findings may also show that restarting the reaction with fresh octanol may partly remove the adsorbed carbonaceous fragments and regenerate the activity.



Scheme 1. Classical dehydrogenation mechanism of alcohol oxidation over Pt metal.

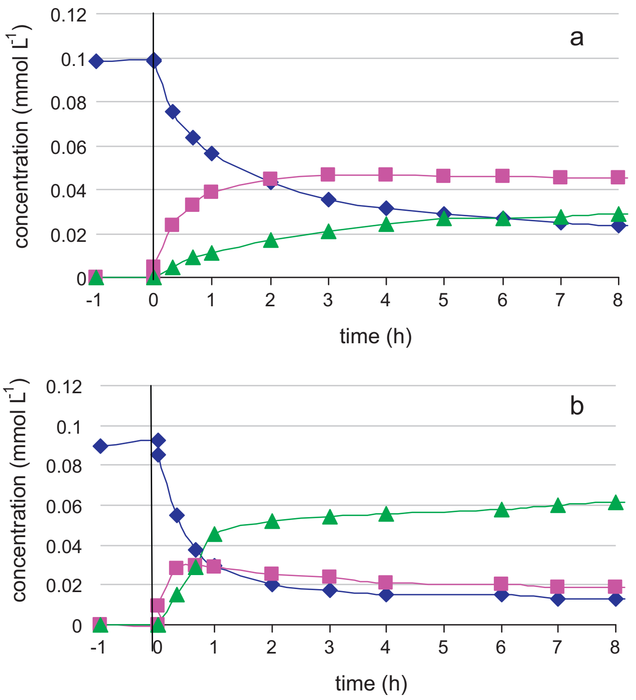


Fig. 6. Oxidation of 1-octanol in dioxane (a) or dioxane/water 50%/50% with addition of 0.03 equiv. NaOH (b) in the presence of 2.5%Pt–0.9%Bi/C. Reaction conditions: 150 mL 0.1 $\text{mol}\,\text{L}^{-1}$ 1-octanol, 100 °C, 10 bar air, 1-octanol/Pt molar ratio = 100, (♦) 1-octanol, (■) 1-octanal, (▲) 1-octanoic acid.

Numerous reports have been published on the improvement of performances of supported Pd and Pt catalysts by promotion with bismuth in terms of overoxidation and stability [44,45]. One reason is that Bi is oxidized more easily than the noble metal, thus maintaining it reduced and active [41]. Thereby a 2.5%Pt-0.9%Bi/C catalyst prepared by redox deposition on platinum was tested. Fig. 6 gives the results for the reactions performed in dioxane or dioxane/water 50%/50% mixtures with addition of 0.03 equiv. NaOH.

In dioxane, substantial oxidation of the 1-octanol was observed under these conditions, with conversion of 43% within 1 h. Then, the oxidation slowed considerably over time. As in the case of Pt/C, the replacement of part of dioxane by water and addition of 0.03 equiv. NaOH increased the initial reaction rate and favoured the formation of the acid. However, though conversion was slightly improved some important slow down of the reaction was still observed and conversion did not go to completion.

Both the unpromoted and promoted catalysts behave similarly, significant improvement of the initial activity being observed with addition of water. However, the catalyst activity of the unpromoted and promoted catalysts was comparable and conversion reached rapidly a stable value.

We also carried out experiments on 2-octanol oxidation in the presence of Pt catalysts promoted by Bi, using two different batches 2.5%Pt–0.9%Bi/C and 2.7%Pt–0.9%Bi/C. The results are shown Fig. 7.

The bimetallic 2.5%Pt–0.9%Bi/C catalyst was slightly more active in dioxane than the unpromoted monometallic 2.8%Pt/C catalyst (40% conversion after 6 h in comparison to 29%). Replacement of 25 vol.% of dioxane by water increased only slightly the initial reaction rate. On the other hand, addition of 50 vol.% of water to the medium increased dramatically the activity of the catalyst, whatever the batch of catalyst.

It has also been reported in the literature that Bi promoter can partially be leached out during reactions performed in acidic solutions, resulting in irreversible catalyst deactivation [45]. This could be excluded in our case, since no Bi ions could be detected by ICP-OES analysis of the final reaction medium.

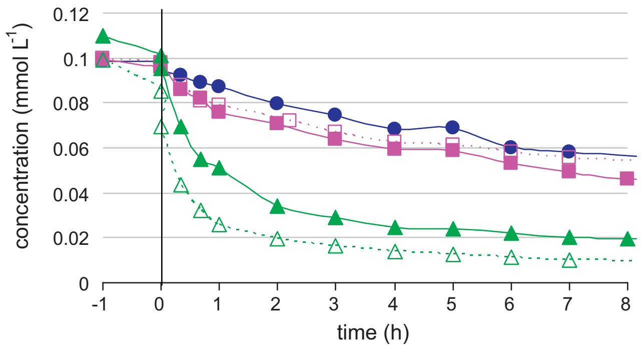


Fig. 7. Promotion effect of water on the catalytic oxidation of 2-octanol to 2-octanone in dioxane/water mixtures in the presence of Pt–Bi/C. Reaction conditions: 2-octanol (0.1 $\text{mol}\,\text{L}^{-1}$), Pt–Bi/C (1 mol.% Pt), solvent (150 mL), 100 °C, 10 bar. (●) dioxane, (■, □) dioxane/water 75%/25%, (▲, △) dioxane/water 50%/50%, (----) 2.5%Pt-0.9%Bi/C, (—) 2.7%Pt–0.9%Bi/C.

3.4. *Promoting effect of water*

Fig. 8 gives the initial reaction rate (expressed as the percentage of conversion of 2-octanol after 1 h) as a function of the volume percentage of water in the solvent, whether Pt/C or Pt–Bi/C catalysts were used. As mentioned before, Bi promotion of the Pt catalyst did not really improve the activity. Under identical reaction conditions, when water is added into dioxane, a substantial increase in the conversion is observed. The highest activity with total conversion within 1 h could be reached from 50 vol.% water, using Pt/C as catalyst.

Similarly, under the same conditions, conversion after 1 h in dioxane for 1-octanol oxidation was 36 and 43% in the presence of Pt/C or Pt–Bi/C catalyst, respectively. Addition of 10 and 50 vol.% of water enhanced rapidly this conversion to 67–73% (Figs. 2 and 6). It should also be pointed out that the primary alcohol reacted initially faster than did the secondary alcohol.

Oxidation of the alcohol produces water. One may think that the water will accumulate on the catalyst surface resulting in a decrease of accessible active sites. However, the carbon surface is rather hydrophobic, since the activation procedure of the used carbon did not significantly introduce polar groups such as carboxylic or phenolic groups. Also, the solvent chosen, dioxane is able to carry large quantities of water. Thus, water when formed should be rapidly removed from the surface and be transferred to the solvent.

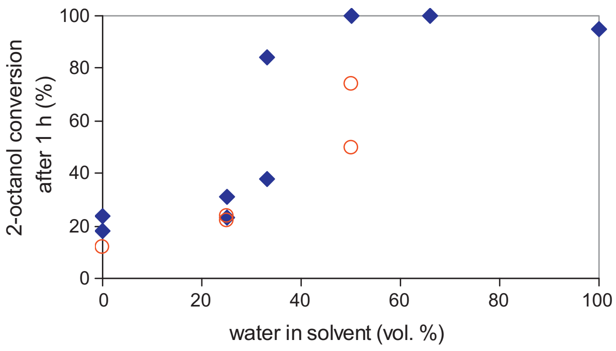


Fig. 8. Conversion of 2-octanol after 1 h reaction as a function of the volumic percentage of water in solvent in the presence of Pt/C (♦) or Pt–Bi/C (○) catalysts. Reaction conditions: 2-octanol (0.1 $\text{mol}\,\text{L}^{-1}$), Pt or Pt–Bi/C (1 mol.% Pt), solvent (150 mL), 100 °C, 10 bar.

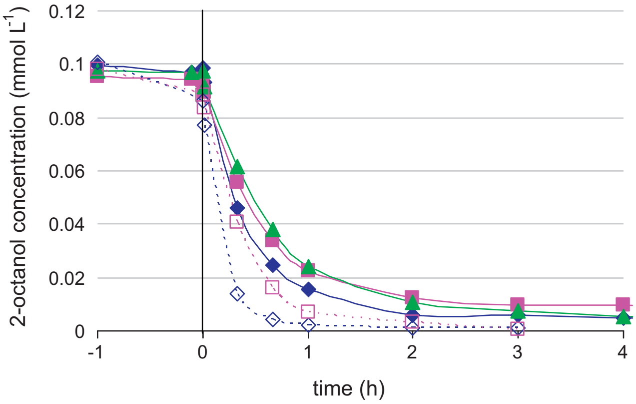


Fig. 9. Oxidation of 2-octanol in the presence of 2-octanone added from the beginning of the reaction. Reaction conditions: 150 mL 0.1 mol L^{-1} 2-octanol, 100 °C, 10 bar, 2-octanol/Pt molar ratio = 100, (♦, ■, ▲) dioxane/water 66%/34% with addition of 0, 15 or 30 mmol L^{-1} 2-octanone, (□, Δ) dioxane/water 50%/50% with addition of 0 or 30 mmol L^{-1} 2-octanone.

A rapid deactivation induced by adsorption of intermediate and by-products has also been reported for oxidation of alcohols. The carbonyl products formed upon oxidation of 1-or 2-octanol could strongly adsorb on the catalyst surface. We examined the possibility of adsorption of the acid (*vide supra*). We also checked the effect of 2-octanone. Mounzer et al. [68] showed that 2-octanone was strongly adsorbed on a 5%Pt–1%Bi/C, very rapidly inhibiting the reaction in heptane or xylene. A 16–18% (v/v) dioxane/heptane solvent corresponding to a minimum in the adsorption coefficient of 2-octanone was suitable for a better desorption of the ketone and a longer activity of the catalyst. In the present case, one may assume that substitution of dioxane with some water will modify the hydrophilicity properties of the solvent, hence facilitating desorption of the ketone from the catalyst surface. Several oxidation reactions of 2-octanol were carried out in which 2-octanone was added in the solution from the beginning of the reaction in dioxane/water to check if the reaction was affected by the formed 2-octanone. The results are shown in Fig. 9 for two compositions of the solvent.

Upon addition of 15 or 30 mol.% of 2-octanone, no significant slow-down of the reaction rate could be noted, whatever the solvent. Hence the adsorption of carbonyl compound could be excluded as the main cause of severe deactivation in dioxane. However, the effect of water may be to enhance the adsorption of the alcohol or the desorption of the carbonyl compound. The alcohol and carbonyl substrates all contain both a polar oxygenated function and a carbon chain with a certain lipophilic character. The solvent used may change the affinity of the substrate and the product for the catalyst surface or the solvent.

Finally, water is also a weak base which may assist the first step of the reaction, i.e. the H-abstraction from the alcohol during the dissociative chemisorption of the alcohol molecule on the catalyst surface, and the subsequent conversion to the carbonyl product in the presence of oxygen. This effect of water was suggested by Anderson et al. [15] and could explain the best performances achieved when water was added into the medium.

4. Conclusions

Platinum supported catalysts are solids that can oxidize aliphatic alcohols with air in both organic and aqueous media. The observed catalyst deactivation for 1-octanol and 2-octanol oxidation was the highest for the primary alcohol. This reaction was relatively fast during the initial stage, before dramatically changing to become constant. Deactivation could be suppressed by performing the reaction in dioxane/water solvent at 60 °C instead of 100 °C, probably by reducing overoxidation or by suppressing decarbonylation and thus strong adsorption of by-products. 2-octanol oxidation was very selective to 2-octanone and gave better yields than 1-octanol, since decarbonylation of ketone is less important. Promotion by Bi does not eliminate the deactivation of Pt.

For both substrates, with increasing water contents in a dioxane/water mixture, a dramatic enhancement of the catalytic activity was observed. The enhancement is likely to be ascribed to the relative affinity of the substrate for the catalyst surface (support) as a function of the polarity of the solvent.

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