Oxidation of 9-decen-1-ol (rosalva) by air in aqueous media on platinum catalysts

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Oxidation of 9-decen-1-ol to 9-decenoic acid was conducted in aqueous media (dioxane–water mixtures) in the presence of supported palladium or platinum catalysts. The beneficial effect on the activity of a bismuth promoter, deposited on the platinum particles by a redox reaction, was demonstrated. Operating in a mass-transport-limited regime improves the resistance of the catalyst to deactivation by over-oxidation.

Oxydation du dec-9-en-1-ol (rosalva) par l'air en milieu aqueux sur des catalyseurs au platine. L'oxydation du dec-9-en-1-ol en acide dec-9-en-1-oïque a été effectuée en mileu aqueux (mélanges dioxane–eau) en présence de catalyseurs au palladium ou platine supportés. Un effet promoteur sur l'activité du bismuth déposé sur les particules de platine par une réaction redox a été démontré. Le fait d'opérer en régime limité par le transport de matière augmente la résistance du catalyseur à la désactivation par suroxydation.

Liquid phase oxidations of organic molecules are usually performed with strong oxidants such as sodium hypochlorite, nitric oxide, permanganate or chromium(VI) reagents. Because of the high cost of these oxidizing agents and their environmental unfriendliness, processes based on mild oxidation reagents or on air oxidation are attractive.[1,2] In the case of oxygenated compounds, oxidation can be carried out catalytically with organic nitroxyl radicals such as 2,2,6,6-tetramethylpiperidin-1-oxyl, commonly known as TEMPO.[2] Oxidations of alcohols can also be carried out with molecular oxygen on noble metal catalysts (platinum or palladium). These reactions have been successfully performed in *n*-heptane, ethyl acetate, 2-butanone and dioxane, but, when possible, water is preferred. The conditions required for this reaction are mild (atmospheric pressure and temperatures in the 20–80 °C range), so this process is useful for the oxidation of carbohydrates.[3–15] It was also applied to the oxidation of simple aliphatic or aromatic alcohols or polyols, and important work on monometallic Pt and Pd catalysts was done and reviewed by Heyns and coworkers.[3–5] Different sugars were oxidized to the corresponding sugar acids and the method was extended to oxidize alcohols, vicinal diols, and polyols. A comprehensive survey on the oxidation of alcohols was published by Mallat and Baiker.[16] An advantage of air oxidation on metal catalysts is that carbon═carbon double bonds do not oxidize or isomerize,[3,4,16] so unsaturated alcohols may be oxidized to the corresponding unsaturated aldehydes or carboxylic acids.

Primary alcohols are oxidized to carboxylic acids with intermediate formation of aldehydes. In aqueous solutions the latter are very reactive, so the reaction proceeds to the acid. However, most unsaturated aliphatic alcohols are oxidized to the corresponding aldehydes with high selectivity, because either the hydroxyl group is located next to an unsaturated site[16] or the reactions were performed in non-aqueous media. Indeed, the generally accepted mechanism is an oxidative dehydrogenation, which implies as a first step the dehydrogenation of the substrate over the metal in the zero-valent state.[17] Therefore, the oxidative dehydrogenation of aldehydes to the corresponding carboxylic acids requires the prior hydration of the carbonyl compound to a geminal diol that is the reactive species in the oxidative dehydrogenation to the corresponding carboxylic acid:

$$\mathrm{CHO} \rightleftharpoons \mathrm{CH(OH)_2} \rightarrow \mathrm{COOH}$$

This hydration reaction cannot occur in organic solvents, so the oxidation of unsaturated alcohols stops at the aldehyde stage. Thus, *trans*-9-octadecenol (elaidyl alcohol), *trans*-2-methyl-2-butenol (tiglyl alcohol), and geraniol were converted to the corresponding unsaturated aldehyde in heptane with high yields over unsupported platinum catalyst.[5] The oxidation of retinol,[18] steroids[19] and chrysanthemyl alcohol in different anhydrous organic solvents[20] was carried out to the corresponding aldehyde or ketone, using high amounts of unsupported or supported platinum catalyst. The oxidation of 3-methyl-2-buten-1-ol in organic solvents at reflux on a PtBi/C catalyst gave higher aldehyde yield by eliminating water *via* azeotropic distillation.[21]

There are few examples of the metal oxidation of unsaturated alcohols to carboxylic acids. The oxidation of cinnamyl alcohol over Pt/alumina catalyst yielded 9% cinnamaldehyde with a selectivity of 88.5% when performed in an aqueous solution containing dodecylbenzenesulfonic acid sodium salt detergent, under transport-limiting conditions. A bismuth-promoted catalyst enhanced the initial rate by a factor of more than 26 and the yield in cinnamaldehyde increased to 94–96%.[16] In contrast, a 36.2% yield in cinnamic acid was reported for the oxidation of cinnamaldehyde in NaOH aqueous solutions over 10% Pd/C catalyst. The addition of complexing agents (sodium salt of EDTA, triethanolamine) increased the yield of isolated acid to 86.9% and allowed recycling of the catalyst.[22] The reason for the formation of the acid in the latter case would be that the dehydrogenation mechanism does not apply and that oxidation involves an oxygen insertion into the aldehyde.[16]

The aim of the present work was to investigate the possibility of preparing 9-decenoic acid by air oxidation of 9-decen-1-ol (Scheme 1) on a palladium or platinum catalyst. 9-Decenoic acid is a synthon used in the preparation of flavor and fragrance ingredients,[23] as well as prostaglandin and its

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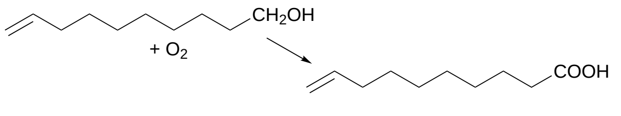

Scheme 1 Oxidation of 9-decen-1-ol to 9-decenoic acid

analogues.[24] This acid is usually prepared by degradation of 10-undecenoic acid or by oxidation of 9-decen-1-ol by strong oxidizing agents, including chromic acid.[24]

Experimental

Palladium and platinum catalysts were prepared by impregnation of active charcoal with acidic solutions of $PdCl_4^{2-}$ and $PtCl_6^{2-}$ ions at room temperature. The reduction was carried out by addition of an aqueous solution of formaldehyde and a 30% KOH aqueous solution. The solids were washed and dried under vacuum overnight. The 4.5 wt% Pt/alumina was a commercial catalyst (Engelhard 4759).

Bismuth-promoted catalysts were obtained by the following procedure.[10] Palladium or platinum catalysts were prereduced in an aqueous solution of glucose under an inert atmosphere. The appropriate amount of $BiONO_3$, dissolved in 1 M HCl, was added into the mixed slurry under a nitrogen atmosphere. Under these conditions, bismuth atoms were deposited on the surface of the metallic particles (M = Pt, Pd) by a redox surface reaction

$$(M{-}H)_{surface} + BiO^+ \rightarrow (M{-}Bi)_{surface} + H_3O^+.$$

The pH was increased to 9 with NaOH, then the catalyst was filtered, washed, and dried under vacuum at 100 °C. The Bi/Pd or Bi/Pt molar ratios of the catalysts prepared were in the range 0.45–0.64. Electron microscopy combined with EDX analyses at 1.5 nm spatial resolution proved that the promoter was uniformly located on the metallic particles.[10]

The oxidations were performed at 50 °C in a 500 cm^3 glass reactor, equipped with condenser, gas inlets (N_2 or air), pH measuring electrode, pO_2 sensor and magnetic stirrer (1500 min^{-1}). A detailed description of the apparatus is presented elsewhere.[10,19] The purity of 9-decen-1-ol by gas chromatography analysis was 98%. The catalyst (1 g) was suspended in a solution of 9-decen-1-ol dissolved in 300 ml dioxane–water, 50:50 to 70:30 and heated to 50 °C while bubbling N_2 through the suspension. The gas supply was then switched to air (0.5 l h^{-1}). The pH of the reaction medium could be kept constant by the addition of a 10% aqueous sodium hydroxide solution with a pump controlled by a pH regulator. Samples were taken at periodic time intervals, acidified, and analyzed by gas chromatography on a FFAP J&W column using octanoic acid as an internal standard. The selectivity to the acid is very high, so the amount of sodium hydroxide added to maintain a constant pH can also be used to measure the conversion of the alcohol.

Results and Discussion

Choice of solvent

9-Decen-1-ol and the corresponding aldehyde and acid are insoluble in water. However, if one wants the alcohol to be oxidized to the carboxylic acid, it is preferable to operate in an aqueous medium to allow the hydration of the intermediate aldehyde. Dioxane and water mixtures were used since they are miscible in all proportions. Homogeneous mixtures containing at least 50% dioxane to dissolve 1.2 wt% of 9-decen-1-ol were employed for the oxidation reaction.

Catalytic oxidation of 9-decen-1-ol on monometallic catalysts

Oxidation experiments were performed using two different supports: hydrophobic active carbon (4.5% Pd/C and 6.35% Pt/C) and hydrophilic alumina (4.5% Pt/Al_2O_3). The pH in all reactions was adjusted to pH 8 (*vide infra*) and the substrate/metal molar ratio was *ca.* 100.

To avoid the over-oxidation of the metal, which is the main cause of catalyst deactivation, the rate of oxygen supply to the catalyst should be regulated with respect to the rate of oxygen consumption.[16] Therefore, the oxidation of 9-decen-1-ol was performed with a very low flow rate (0.5 l h^{-1}) to minimize the actual concentration of dissolved oxygen.

The conversion of 9-decen-1-ol to 9-decenoic acid with time, calculated from the amount of NaOH consumed and from gas chromatography analysis, is given in Fig. 1 for 4.5% Pd/C, 6.35% Pt/C and 4.5% Pt/Al_2O_3. The monometallic catalysts were initially weakly active, but deactivation rapidly occurred. The reaction stopped at only 20% conversion with the palladium catalyst after 23 h of reaction, but 50% conversion could be achieved with the platinum catalysts. Platinum catalysts are less poisoned by over-oxidation than palladium, because of the higher redox potential of platinum.[25] A small effect of the Al_2O_3 support was noted. Indeed, after 30 h, the conversion was 50% on 4.5% Pt/Al_2O_3, whereas it was only 32% on 6.35% Pt/C. The better performance of the alumina-supported catalyst may be attributed to a higher metallic surface area or to a higher purity. Replacing temporarily the air flow by a nitrogen flow to try to reactivate the 6.35% Pt/C catalyst had only a minor influence on the conversion. The yield of the intermediate aldehyde was very low (only a few percent at the very beginning of the reaction) and the acid was the main product of the reaction. The partial pressure of oxygen in the reaction medium measured during these experiments is shown in Fig. 2. In the case of the monometallic catalysts, the concentration of oxygen increased smoothly and saturation was attained within two hours in spite of the low air flow rate. This indicates a low reaction rate and suggests a rapid deactivation of the catalyst.

Catalytic oxidation of 9-decen-1-ol on bimetallic catalysts

Bismuth-promoted palladium and platinum catalysts were employed to cope with the deactivation problem. Indeed, it has been shown in the literature that in case of deactivation, promotion by Bi, Pb or other heavy metals improved the performance (activity, selectivity) of catalysts. For instance, the activity of palladium for glucose oxidation was dramatically enhanced by bismuth addition.[10,26] The results were interpreted in terms of bismuth adatoms preventing oxygen poisoning of the palladium surface, because of their stronger

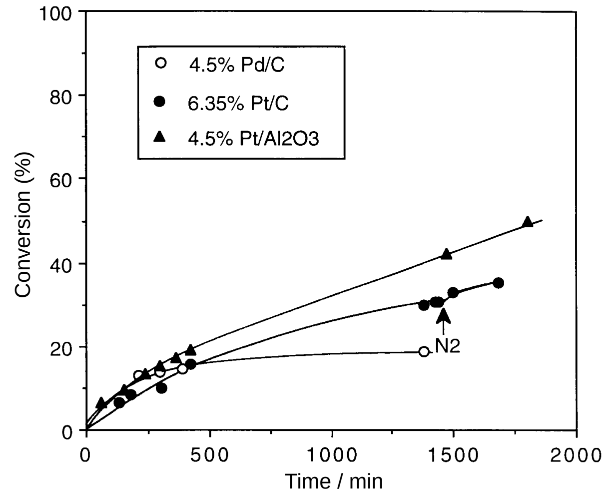

Fig. 1 Conversion of 9-decen-1-ol on Pd and Pt supported catalysts in a 50:50 dioxane–water solvent. Temperature 50 °C, 23 mmol 9-decen-1-ol, 1 g catalyst, 300 ml solvent, air flow rate 0.5 l h^{-1}, pH maintained at 8

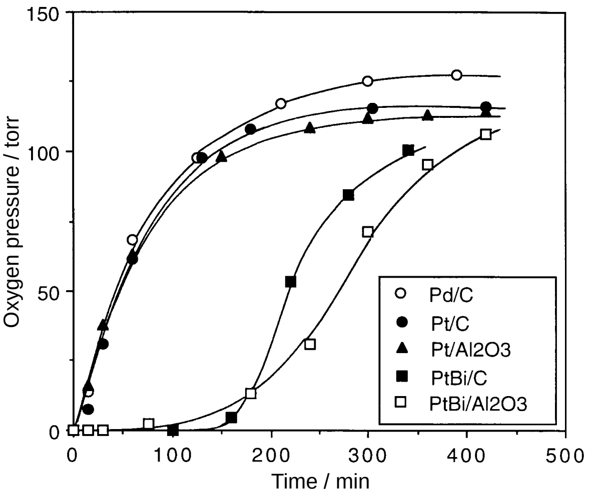

Fig. 2 Partial pressure of oxygen in the reaction medium during the oxidation of 9-decen-1-ol

affinity for oxygen.[10] Cinnamyl alcohol was oxidized to cinnamaldehyde with 88.5% selectivity at 10% conversion on Pt/Al_2O_3 in an aqueous solution containing an anionic surfactant; however, on $PtBi/Al_2O_3$ catalysts with different Bi/Pt ratios, the cinnamaldehyde selectivity was > 93% at 83% conversion.[27] The yield in acetophenone after oxidation of 1-phenylethanol in an aqueous alkaline solution was less than 20% with unpromoted Pt/Al_2O_3, whereas total conversion could be reached with a PtBi catalyst.[28]

In the oxidation of 9-decen-1-ol, the activity of the promoted palladium catalyst 5.07% Pd–2.93% Bi/C (Bi/Pd = 0.58) did not change compared to the nonpromoted catalyst, whereas the addition of bismuth to the platinum catalysts increased the rate dramatically. Reaction data obtained with the 6.3% Pt–2.9% Bi/C catalyst (Bi/Pt = 0.45) are given in Fig. 3. The 5.07% Pt–2.93% Bi/Al_2O_3 (Bi/Pt = 0.52) catalyst gave similar data. Oxidation of 9-decen-1-ol was completed within 6 h, yielding essentially 9-decenoic acid. The initial reaction rates (*ca.* 60 mol h^{-1} mol_{Pt}^{-1}) are not representative of the kinetic activity, because the oxidation reactions were performed in a mass-transfer-limited regime. Indeed, the oxygen pressure in the reaction medium was zero during the oxidation, except at the very end of the reaction (Fig. 2). By promoting the platinum catalyst with bismuth, steady-state conditions could be obtained due to a balance between the dehydrogenation steps and the subsequent oxidation of the surface hydrogen species by adsorbed oxygen.

Influence of pH

The effect of pH on the oxidation of 9-decen-1-ol to 9-decenoic acid over Pt–Bi/C is presented in Fig. 3 and 4. If not adjusted, the initial pH of 4.4 decreased slowly due to the formation of decenoic acid. In that acidic medium, a strong inhibition of the oxidation process was noted from the start and the reaction stopped after 20% conversion (Fig. 4). Under alkaline conditions (pH regulated by addition of 10% NaOH), the oxidation was smooth and all the 9-decen-1-ol was oxidized selectively to the acid (Fig. 3). The low reaction rate in acidic medium is attributed to the adsorption of molecular carboxylic acid on the catalyst surface. This deactivation can be easily circumvented by addition of sodium hydroxide to the reaction medium to convert the acid to the sodium salt, which does not adsorb on the metal. The need for a slightly alkaline pH to perform oxidation reactions leading to acidic products was previously noted in the oxidation of glucose to gluconic acid,[13,29] of propan-1-ol to propionic acid,[30] and of glycerol to glyceric acid,[31] tartronic or mesoxalic acids.[32–34] In acidic medium, bismuth may also be leached from the catalyst.

Influence of air flow rate

At a low flow rate of air (0.5 l h^{-1}), it was possible to oxidize the alcohol to the corresponding acid on a PtBi catalyst. We verified that operating in a diffusion-limited supply of oxygen was mandatory by applying a higher flow rate of gas (7 l h^{-1}). Experiments were carried out with a 70:30 dioxane–water mixture. Fig. 5 compares the yields in 9-decen-1-ol and 9-decenoic acid (Fig. 5a) and the oxygen concentration measured in the reaction medium (Fig. 5b) during these two experiments. At the low flow rate, the reaction rate was slightly lower than that obtained in the 50:50 dioxane–water solvent, and a deactivation was observed at the end of the oxidation. This indicates that the increase in the proportion of dioxane has a small negative effect on the reaction rate. Nevertheless, the reaction was still under mass transfer control and the oxidation was completed within a few hours. At the higher air flow rate, the concentration of oxygen in the reaction medium increased rapidly to saturation and the reaction, which started with a rather high initial rate, slowed down. The decreased rate is attributed to the over-oxidation of the Pt^0 active sites, due to the high oxygen concentration at the catalyst surface relative to the rate of its consumption by the surface reaction.

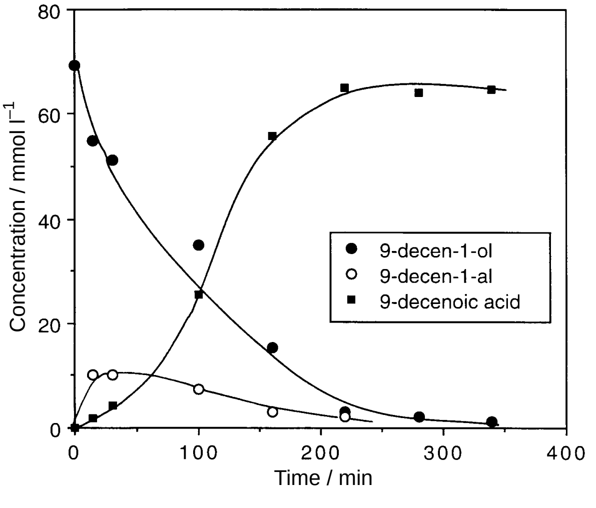

Fig. 3 Oxidation of 9-decen-1-ol on 6.3% Pt–2.9% Bi/C (molar ratio Bi/Pt = 0.45) at pH adjusted to 8. Temperature 50 °C, 23 mmol 9-decen-1-ol, 1 g catalyst, 300 ml 50:50 dioxane–water, air flow rate 0.5 l h^{-1}

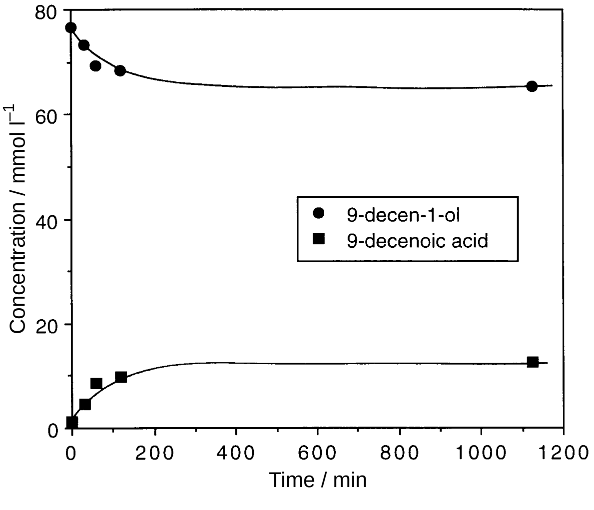

Fig. 4 Oxidation of 9-decen-1-ol to 9-decenoic acid on PtBi/C catalyst without pH control. Temperature 50 °C, 23 mmol 9-decen-1-ol, 1 g catalyst, 300 ml 50:50 dioxane–water, air flow rate 0.5 l h^{-1}

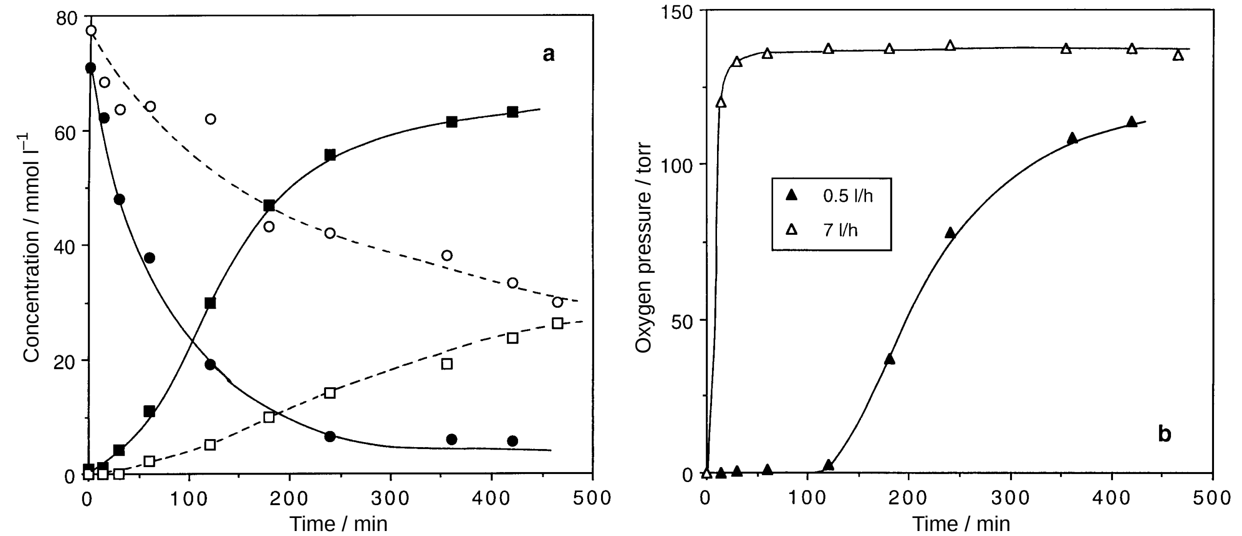

Fig. 5 Influence of the air flow rate during oxidation of 9-decen-1-ol in 70:30 dioxane–water. (a) Concentration of alcohol (● 0.5 l h^{-1}, ○ 7 l h^{-1}) and acid (■ 0.5 l h^{-1}, □ 7 l h^{-1}) with time. (b) Oxygen pressure in the reaction medium (▲ 0.5 l h^{-1}, △ 7 l h^{-1})

Influence of the C=C double bond

The oxidation of 9-decen-1-ol was very slow on Pt/C, as mentioned before. In order to determine the influence of the double bond on the reaction rate, the oxidation reactions of decan-1-ol and 9-decen-1-ol were compared on a 6.58% Pt/C catalyst under the same conditions (controlled pH of 8, air flow rate of 0.5 l h^{-1}). The progress of the reaction was followed by the consumption of sodium hydroxide. Conversion data are given in Fig. 6 for both substrates. These data clearly show that the presence of the C=C bond in the alkyl chain has an adverse effect. Whereas the oxidation of decanol proceeded to near completion, only 25% conversion of 9-decen-1-ol could be obtained within the same time. By adsorbing strongly on the metal, the C=C bond prevents the adsorption and dehydrogenation of the alcohol function, which also takes place on surface Pt atoms. The bismuth addition to platinum may greatly decrease the adsorption of the C=C bond, resulting in an increase of the overall rate of oxidation of the alcohol. This is in agreement with the theoretical calculation of Delbecq and Sautet showing that alloying a Group 10 metal with a more electropositive element increases the four-electron repulsions and thus strongly decreases the adsorption of C=C bonds.[35]

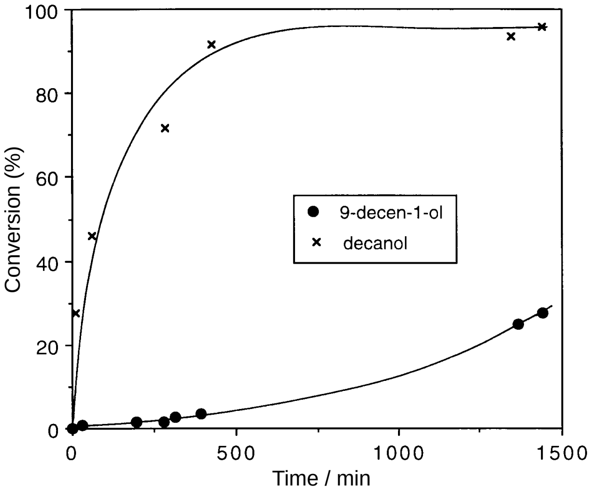

Fig. 6 Comparison of the oxidation of decan-1-ol and 9-decen-1-ol on 6.58% Pt/C: conversion into acid with time calculated from the NaOH consumption. Temperature 50 °C, 23 mmol substrate (● 9-decen-1-ol, × decan-1-ol), 1 g catalyst, 300 ml 50:50 dioxane–water, air flow rate 0.5 l h^{-1}

The generally accepted dehydrogenation mechanism of the alcohol implies the transient presence of hydrogen on the catalyst surface, which was confirmed by the measurement of the catalyst potential during oxidation of alcohols.[36] This hydrogen is continuously oxidized by air, but a hydrogenation of the C=C bond in the 9-decen-1-ol or 9-decenoic acid might be expected. However, decanol and decanoic acid were never observed in significant amounts by GC analysis, suggesting that, upon dehydrogenation of the alcohol, the oxidation of hydrogen is very rapid with respect to the hydrogenation of the C=C bond.

Oxidation of 9-decen-1-ol in suspension in water

The above experiments were performed with dilute solutions of 9-decen-1-ol in dioxane–water mixtures, to allow us to follow the progress of the reaction with GC. In spite of the insolubility of 9-decen-1-ol in water, it was verified that the reaction was possible by stirring a 10 wt% suspension of 30 g of 9-decen-1-ol in water, using 2 g of 4.58% Pt–2.95% Bi/C and a low air flow rate. From the amount of NaOH solution consumed to neutralize the acid formed, a yield of 70% acid was measured after 50 h of reaction. The final reaction mixture was filtered, acidified with HCl, and the organic compounds were extracted with dichloromethane for GC analysis. The nearly complete conversion of the alcohol and the formation of high yields of acid were confirmed (*ca.* 83%, not very far from the value calculated from the amount of NaOH). Some byproducts (*ca.* 14 %) were observed, which were not detected in dilute dioxane–water solutions.

Conclusion

The first attempt to oxidize 9-decen-1-ol to 9-decenoic acid by air on supported metal catalysts in dioxane–water mixtures was successful (selectivity >83% at complete conversion). The deactivation of the platinum catalysts by strong adsorption of the C=C bond and by over-oxidation could be avoided by Bi deposition onto the platinum particles and by controlling the air flow rate to carry out the reaction in an oxygen-limited regime. This process, in spite of the low productivity (8.5 mol h^{-1} mol_{Pt}^{-1}), can match stoichiometric oxidation processes and could be well-suited to prepare unsaturated oxygenated intermediates for which strong oxidizing agents are not appropriate.

Acknowledgements

The authors kindly acknowledge Firmenich SA for supplying 9-decen-1-ol and 9-decenoic acid.

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Received 4*th July* 1997; *Paper* 7/08337H