



## 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.

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### 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<sub>x</sub>/CeO<sub>2</sub> catalyst showed high activity at room temperature and atmospheric O<sub>2</sub> 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  $\alpha$ -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<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub> has also been proposed as an alternative solvent [62–66]. Thus, over Pd/Al<sub>2</sub>O<sub>3</sub>, 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<sup>-1</sup> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> [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<sub>2</sub> 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<sub>3</sub> 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 CuK $\alpha$  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  $\times$  0.25 mm, 0.25  $\mu$ m 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 <sup>1</sup>H NMR to determine the content in reactant and products.

<sup>1</sup>H NMR data were conform to the literature:

2-Octanol (<sup>1</sup>H NMR, 250 MHz, CDCl<sub>3</sub>):  $\delta$  3.80 (m, 1 H);  $\delta$  1.83 (s, 1 H);  $\delta$  1.40 (m, 10 H);  $\delta$  1.18 (d, 3 H, *J*<sub>ab</sub> = 6.1 Hz);  $\delta$  0.86 (t, 3 H, *J*<sub>ab</sub> = 6.2 Hz).

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