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Oxidation of primary alcohols with air on carbon-supported platinum catalysts for the synthesis of aldehydes or acids

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Abstract

Carbon-supported platinum catalysts were shown highly efficient heterogeneous catalysts for the selective oxidation of various types of primary alcohols to the corresponding aldehydes and carboxylic acids, using a low pressure of air and a temperature of 100 °C. Especially, alcohols could be oxidized to afford the aldehyde in high yields in dioxane, whereas the carboxylic acid was selectively produced in dioxane/aqueous solution mixtures or dioxane/alkaline aqueous solution mixtures. The dispersion of the platinum catalyst was dependent on the carbon activation treatment and on the method of preparation and it influenced significantly the activity and the resulting selectivity. The platinum catalyst prepared by impregnation of CO_2-activated carbon showed the best results compared to platinum catalysts prepared on air-activated carbon or by cationic exchange.

Keywords: Selective; Oxidation; Air; Primary alcohols; Carbon-supported platinum catalysts

1. Introduction

The selective oxidation in liquid phase of alcohols provides an access to aldehydes, carboxylic acids and ketones. It is a very important transformation in the field of fine chemicals and pharmaceutical intermediates. Many oxidizing reagents have been developed for the oxidations of this type. Unfortunately, most of these stoichiometric oxidants (hypochlorites, high-valent metal oxidation agents such as chromates and active manganese dioxide, mineral acids) are often used in halogenated organic solvents, and produce relatively large amounts of hazardous or toxic wastes. The disposal of metal wastes or the isolation of the products is a serious drawback for economical and environmental benefits. Therefore, there is an increasing demand for the development of atom efficient catalytic methods that use clean oxidants [1]. Air (or molecular oxygen) is an especially attractive oxidizing agent because it is readily available, inexpensive and non-toxic [2–4]. Oxidation with homogeneous catalytic systems (Pd, Cu, Co, Ru compounds) using molecular oxygen has been much studied [5]. But most of these systems require the presence of bases and additives [6,7], special solvents, or large quantities of a co-oxidant such as reactive aldehydes that forms peracids which are the actual oxidizing agents [8]. Few catalytic systems are employing air as sole oxidant. Nitroxyl-based systems combining $RuCl_2(PPh_3)_3$ and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) have been reported [9]. There are some examples of solid catalysts in aerobic oxidation of alcohols based on supported or immobilised platinum group metals. Polymer-supported Pd species [10], Pd(II)- or Ru(III)-hydrotalcite [11,12], Pd(II) [13] and Ru(III)-exchanged hydroxyapatite [14,15], zeolite confined nanoparticles of RuO_2 [16], Ru/Al_2O_3 [17] and Ru/TiO_2 [18] were reported to be active for the oxidation of alcohols with molecular oxygen. Some of these catalysts are particularly efficient, such as $PdCl_2(PhCN)_2$ immobilised on hydroxyapatites, with TON's up to 236 000 being reached in a solvent-free oxidation of 1-phenylethanol [19]. Platinum and palladium supported on carbon have been used at room temperature for the oxidation in aqueous phase of sensitive compounds including carbohydrates and their derivatives [20,21]. Gold catalysts have also received recent attention [22]. These catalytic systems are active for benzylic and allylic oxidation, but also for aliphatic and heterocyclic alcohols. Nevertheless, most of them were developed for the selective oxidation of alcohols to aldehydes.

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In this work, attention was focused on Pt-catalysed oxidation of primary alcohols and on the conditions which will afford either the corresponding aldehyde or the acid with high yield, using the same platinum catalyst. Moreover, supported metallic Pd/C or Pt/C catalysts have been often limited to the oxidation of water-soluble substrates. The oxidation of water-insoluble substrates has little been studied, because for safety reason most organic solvents should not be used in the presence of oxygen and metal catalysts. In this paper, we addressed the problem of oxidation of water-insoluble alcohols to demonstrate that oxidation with carbon-supported platinum catalysts is not limited to water-soluble alcohols. In the previous literature, a water/surfactant system was adapted for the selective oxidation of cinnamylalcohol to the aldehyde over Pt–Bi/Al_2O_3 [23]. Also, the conversion of 9-decen-1-ol to 9-decenoic acid was performed in a 50/50 vol.% dioxane/water mixture at 50 °C [24]. High throughput screening of supported platinum group metal catalysts has been performed in toluene and xylene to oxidize various alcohols to the corresponding carbonyl compounds [25]. The use of supercritical CO_2 as solvent has also been reported as an attractive solution [26]. Previously, we have shown that carbon-supported platinum catalysts may quantitatively oxidize benzyl alcohol to the corresponding aldehyde or acid and concluded that the choice of the solvent was crucial for the selectivity [27]. The application of the alcohol oxidation method was extended to obtain oxidation products that are important building blocks in pharmaceutical industry. Thus, 4-chlorobenzaldehyde is used in the manufacture of baclofen (GBAB receptor agonist) [28], of chlormezanone (centrally acting muscle relaxant) or of chloropyramine (antihistamine). 4-Isopropylbenzoic acid can be used to synthesize nateglinide (insulinotropic agent) [29]. Pralidoxime iodide and obidoxime chloride (antidotes against organophosphorous nerve agents) are derivatives of 2- and 4-pyridinecarboxaldehyde, respectively [30,31]. Picolinic acid (2-carboxypyridine) is used in making local anestehesics such as mepivacaine or bupivacaine hydrochlorides, while isonicotinic acid (4-carboxypyridine) is used for the synthesis of nialamide (antidepressant) [32,33]. 2-Butyl-5-chloro-3*H*-imidazole-4-carboxaldehyde is an important intermediate in the synthesis of Losartan-K used in the treatment of hypertension [34].

2. Experimental

2.1. Carbon supports

The synthetic carbons used as supporting material were phenolic resin-based, spherical activated carbons supplied by MAST [35]. The non-activated carbon material was prepared by carbonisation at 800 °C of a polymeric resin prepared from Novolac resin and hexamethylenetetramine in ethyleneglycol. In order to increase the surface area and pore volume, the raw carbon was post-treated by two different “burn-off” techniques with *x*% burn-off, using either CO_2 at 850 °C (carbon C_{xC}), or air at 450 °C (carbon C_{xA}). In order to introduce oxygen functionalities for the platinum salt exchange, the C_{xC} carbons were submitted to liquid phase oxidation with NaOCl solutions (ca. 3% active chlorine) and were noted C_{xCox}.

Boehm titration of the carbons was performed to measure the acidic oxygen functionalities with bases of different strength: $NaHCO_3$ (carboxylic), Na_2CO_3 (carboxylic and lactones), NaOH (phenols, carboxylic and lactones) [36]. Weighed amounts of carbon samples (0.3 g) were equilibrated with gentle agitation in 25 ml of 0.05 M solutions of the bases. After 48 h at room temperature, the suspensions were filtrated and the solutions were back-titrated with 0.1 M HCl solutions.

Carbons C_{xCox} were optionally calcined in argon at 500 °C to afford $C_{xCox/Ar}$, a treatment that selectively eliminates the thermally unstable carboxylic groups and preserves the phenolic groups.

2.2. Platinum catalyst preparation

Platinum loading (nominal 3 wt.% Pt) was performed by conventional methods, either by ion-exchange using tetra-ammineplatinum chloride and reduction under hydrogen (catalyst Pt_{ex}/C_{xCox} or Pt_{ex}/C_{xA}) or by impregnation with hexachloroplatinic acid followed by liquid phase formaldehyde reduction (Pt_{imp}/C_{xC} or Pt_{imp}/C_{xA}). Cationic exchange was performed on 9.5 g of carbon in suspension in 100 ml of 1 M NH_3 solution under nitrogen at room temperature. After 2 h, a solution of $Pt(NH_3)_4Cl_2\cdot H_2O$ in 1 M NH_3 solution was added dropwise. After stirring under nitrogen overnight, the suspension was filtered and washed until neutrality. The solid was dried under N_2 at 100 °C, and reduced in H_2 flow (250 ml min^{-1}, heating rate 1 °C min^{-1} up to 300 °C, 2 h at 300 °C), before purging in Ar and passivation in 1% O_2 in N_2 for 30 min. In the impregnation method, an aqueous solution of H_2PtCl_6 containing the required amount of platinum was added dropwise under stirring to an aqueous suspension of the carbon. After 5 h impregnation, the slurry was cooled down in an ice bath and a 37 wt.% solution of formaldehyde was added dropwise, and then a 30 wt.% KOH solution. After stirring under nitrogen overnight, the suspension was filtered, washed with water. The catalyst was dried under nitrogen atmosphere at 100 °C for 1 day. An alternative reduction protocol of the exchanged catalyst was the pre-heating of the catalyst precursor in air (250 ml min^{-1}) at 250 °C (1 °C min^{-1}) during 30 min to decompose the metal precursor complex before the reduction in hydrogen (Pt_{ex}/C_{xCox}/calc or $Pt_{ex}/C_{ox/Ar}$/calc).

The platinum content was determined by analysing the solution by ICP, after dissolution of the solid in $H_2SO_4 + HNO_3$ at 250–300 °C, then HCl.

Platinum dispersion was determined by volumetric CO chemisorption at 35 °C using a Micromeritics ASAP 2010M apparatus, assuming a CO/Pt stoichiometry of 1. Transmission electron microscopy (TEM) studies of the catalysts were conducted using a JEOL 200EX microscope.

2.3. Oxidation reactions

All the used reagents were commercial products of analytical grade and were used without further treatment.

Liquid phase oxidation experiments were conducted in two different reactors. In the 250 ml static autoclave with a magnetically driven mechanical stirring, after purging with argon, a solution of 50–100 mmol l^{-1} of the alcohol in 100 ml solvent was stirred in presence of 1 g catalyst and heated to 100 °C. When the reaction temperature was attained, the autoclave was pressurized with air, which corresponded to time zero. Samples of the product mixture were taken from the reactor by means of an internal 1/16 in. tube connected to a valve. In a reactor of 30 ml, stirred with a magnetic barrel and used in order to provide rapid comparisons, the conditions were the same and no sampling was performed during the reaction, but the final reaction mixture was recovered for analysis.

Analysis of the alcohol and oxygenated products in the liquid samples withdrawn from the reactor during the experiments was performed by GC with a DB5 type column (30 m, 0.32 mm, 0.25 μm) after calibration with an external standard. In some experiments the reaction product was isolated and analysed by ^{1}H NMR analysis in d^6-DMSO or D_2O, after filtration of the reaction mixture with an hydrophobic PTFE (0.45 μm) filter, washing with the appropriate solvent and removal of solvent under vacuum.

3. Results and discussions

3.1. Characterization of the carbons

The carbon particles are regular spherical activated carbons with particle sizes in the range 90–125 μm. The characteristics and analysis of the oxygenated functionalities of the samples are given in Table 1.

The specific surface areas of C_{38C} and CC_{47A} were 1220 and 750 $m^2 g^{-1}$, respectively with an average mesopore size of 18 nm. Upon activation, both mesoporosity and microporosity were developed, but the average mesopore size of 18 nm was not changed [37].

The oxygen functionality of the inactivated carbon is very poor and is only constituted by phenolic compounds. Oxidation by NaOCl introduces both lactonic and carboxylic groups. The air oxidized sample contains significant quantities of the different oxygenated functions.

3.2. Oxidation of benzyl alcohol to benzaldehyde or benzoic acid

The choice of the solvent was guided by taking into consideration the generally accepted mechanism for oxidation of alcohols by noble metals. It is a stepwise oxidative dehydrogenation involving a first dehydrogenation of the adsorbed alcohol on the metal surface leading to the aldehyde; then if water is present in the system, the aldehyde intermediate is hydrated to generate a geminal diol which is further dehydrogenated to produce the carboxylic acid. As a result, primary alcohols yield mainly the acids in an aqueous medium, particularly under basic conditions. In the case of benzylic and allylic alcohols where the primary hydroxyl group is located next to an aromatic ring or a C=C bond, the formation of the hydrated form of the corresponding aldehydes is unlikely so that the oxidation stops at this stage and aldehydes are obtained in good yields [21,4].

Whenever the aldehyde is wanted as oxidation product the reaction medium should prevent that small quantities of water formed by the oxidative dehydrogenation of the alcohol remain on the catalyst surface. In contrast when the acid is targeted, the reaction medium should be able to carry large quantities of water to favour the hydration of the aldehyde. Dioxane was chosen to achieve these goals.

Catalyst 2%Pt_{imp}/C_{35C} was initially employed in the oxidation of benzyl alcohol (100 mmol l^{-1}) [27]. Our recent studies [27] showed that the oxidation proceeded smoothly in dioxane in the presence of 1 g of 2%Pt_{imp}/C_{35C} catalyst at 100 °C and 10 bar air pressure to afford benzylaldehyde in very good yield, with a total conversion of benzyl alcohol after 7 h (Table 1). Upon prolonged reaction time, benzaldehyde formed was hardly oxidized to benzoic acid. On the other hand, when the oxidation was carried out in 50/50 vol.% dioxane/water and even better, in 50/50 vol.% dioxane/alkaline solution at pH 9.3, the hydration of benzaldehyde was favoured. As a result, a high yield in benzoic acid was obtained (Table 1). The very high selectivity to benzaldehyde in dioxane can be explained by the conjugation of the C=O group of the aldehyde with the aromatic ring, but also by the nature of the solvent. Dioxane would remove water that is generated during the oxidation of benzyl alcohol and would prevent deactivation of the catalyst as well as further oxidation of the aldehyde to the corresponding carboxylic acid.

Table 1
Textural properties and surface oxygenated groups of parent and modified carbons

Sample of carbon	S_{BET} ($m^2 g^{-1}$)	Pore volume (ml g^{-1})	Elemental analysis		Total acid sites	Boehm titration (mmol g^{-1}_{carbon})		
			N (%)	O (%)		Phenolic	Lactonic	Carboxylic
C	540	0.6						
C_{38C}	1220	1.1	0.60	4.7				
C_{39C}					0.32	0.32	0	0
C_{39Cox}					1.83	0.99	0.34	0.5
$C_{39Cox/Ar}$					1.44	1.03	0.32	0.09
C_{47A}	750	0.8						
C_{39A}					3.17	1.6	0.7	0.87
C_{39Aox}			0.57	25.4	4.37	1.88	0.85	1.64

3.3. *Influence of the activation treatment of the carbon*

The influence of the activation treatment of the carbon support on the catalytic performances of platinum catalysts was studied by comparing catalysts $2\%Pt_{imp}/C_{44A}$ and $2\%Pt/C_{35C}$ prepared by impregnation of carbons C_{44A} and C_{35C}. Table 2 gives the Pt dispersion, the particle size distribution and the catalytic activity and selectivity measured under standard conditions at 100 °C and 10 bar air, in both solvents dioxane and 50/50 vol.% dioxane/aqueous NaOH solution pH_i 9.3.

The platinum experimental loading for both catalysts prepared by impregnation was 2% instead of the 3 wt.% nominal value. Their dispersion measured by CO chemisorption was comparable (35% and 44% for $2\%Pt_{imp}/C_{44A}$ and $2\%Pt_{imp}/C_{35C}$, respectively) in agreement with the mean particle size determined by TEM (3.0 and 2.5 nm, respectively). When the reaction was performed in dioxane, that is to say under the conditions favourable for the selective oxidation to benzaldehyde, both catalysts behave similarly, with comparable initial reaction rate, total conversion of benzyl alcohol within 6–7 h and a very good selectivity to benzaldehyde at total conversion of the alcohol (95% and 98%, respectively). Longer reaction times did not significantly convert benzaldehyde to benzoic acid (only 11% and 14% benzoic acid after 23 h, respectively). On the other hand, when the reaction was performed in dioxane/alkaline aqueous solution, the conversion of the alcohol to the aldehyde was complete within 2 h. But after 23 h of reaction, whilst benzaldehyde was totally oxidized to the acid on $2\%Pt_{imp}/C_{35C}$, only 46% of benzoic acid was measured on $2\%Pt_{imp}/C_{44A}$. This is better illustrated in Fig. 1, giving the concentration profiles as a function of time. These results suggest that Pt catalysts prepared by impregnation of CO_2-activated carbons are more efficient.

The differences in the rate of benzaldehyde oxidation to benzoic acid may be ascribed to the different hydrophilicity of both catalysts. The presence of polar groups on the surface of the air-activated carbon (phenolic, carboxylic groups as determined by Boehm titration) makes catalyst $2\%Pt_{imp}/C_{44A}$ more hydrophilic. Water is then strongly retained on the catalyst surface and may act as a poison of the catalyst. In contrast, C_{35C} with little polar groups will develop an hydrophobic surface repelling water from the solid.

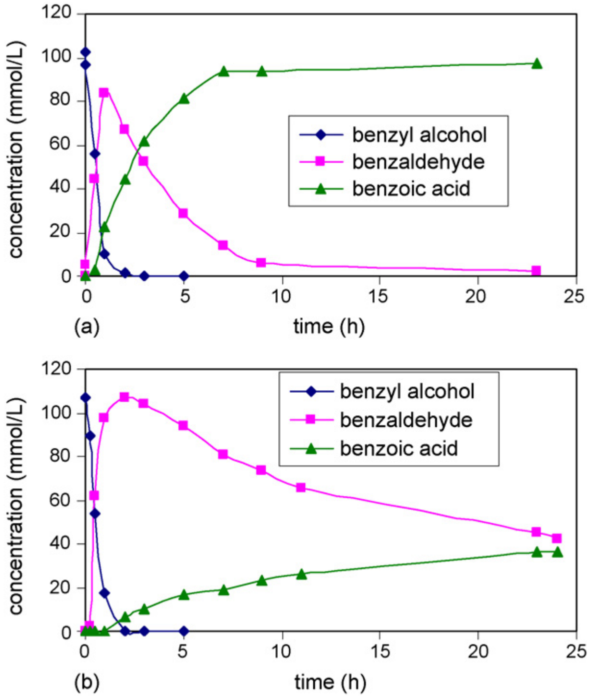


Fig. 1. Oxidation of benzyl alcohol in the presence of (a) $2\%Pt_{imp}/C_{35C}$ and (b) $2\%Pt_{imp}/C_{44A}$ in dioxane/aqueous solution of NaOH 50/50 vol.%.

Table 3 gives the results obtained in the presence of platinum catalysts prepared by cationic exchange. Both supports C_{39A} and C_{38Cox} have oxygen functionalities with a good exchange capacity (2.7% and 3% Pt, respectively).

Surprisingly, catalyst $3\%Pt/C_{38Cox}$ showed a low activity, and only 40% of benzoic acid were formed after 23 h of reaction. This low activity is certainly related to the surprisingly low dispersion (7%). In an attempt to improve the activity of the catalyst, we examined in more detail the influence of the oxygen surface groups on the final platinum dispersion of the catalysts obtained by cationic exchange. The catalyst $3\%Pt_{ex}/C_{38Cox}$ was prepared by cationic exchange of a CO_2-activated carbon C_{38Cox}, further oxidized with NaOCl to introduce

Table 2
Oxidation of benzyl alcohol (Bz-ol) to benzaldehyde (Bz-al) and benzoic acid (Bz-oic) in the presence of platinum catalysts prepared by impregnation

Catalyst	Dispersion (%)	Mean particle size (TEM)	Initial rate of conversion of benzyl alcohol ($mol\,h^{-1}\,mol_{Pt}^{-1}$)	Bz-ol conversion (%)/reaction time (h)	Selectivity in Bz-al (%)/reaction time (h)	Selectivity after 23 h of reaction	
						Bz-al (%)	Bz-oic (%)
Solvent dioxane							
$2\%Pt_{imp}/C_{44A}$	35	3.0	51	100/6	95/6	89	11
$2\%Pt_{imp}/C_{35C}$	44	2.5	63	99/7	98/7	86	14

Catalyst	Dispersion (%)	Mean particle size (TEM)	Initial rate of conversion of benzyl alcohol ($mol\,h^{-1}\,mol_{Pt}^{-1}$)	Bz-ol conversion (%)/reaction time (h)	Selectivity after 23 h of reaction	
					Bz-al (%)	Bz-oic (%)
Solvent dioxane/alkaline water pH_i 9.3						
$2\%Pt_{imp}/C_{44A}$	35	3.0	89	100/2	54	46
$2\%Pt_{imp}/C_{35C}$	44	2.5	93	100/2	2	98

Reaction conditions: Bz-ol 0.1026 $mol\,l^{-1}$, 1 g catalyst, 100 ml solvent, $T = 100\,°C$, $P_{air} = 10$ bar.

Table 3
Oxidation of benzyl alcohol (Bz-ol) to benzaldehyde (Bz-al) and benzoic acid (Bz-oic) in the presence of platinum catalysts prepared by cationic exchange

Catalyst	Dispersion (%)	Mean particle size (TEM)	Initial rate of conversion of benzyl alcohol ($\mathrm{mol\,h^{-1}\,mol_{Pt}^{-1}}$)	Bz-ol conversion (%)/ reaction time (h)	Selectivity after 23 h of reaction	
					Bz-al (%)	Bz-oic (%)
Solvent dioxane						
$2.7\%\mathrm{Pt_{ex}/C_{39A}}$	20	4.2	7	94/23	92	8
$3\%\mathrm{Pt_{ex}/C_{38Cox}}$	7	12.5	7	91/23	93	7
Solvent dioxane/alkaline water pH_i 9.3						
$2.7\%\mathrm{Pt_{ex}/C_{39A}}$	20	4.2	35	100/4	61	39
$3\%\mathrm{Pt_{ex}/C_{38Cox}}$	7	12.5	49	100/4	60	40

Reaction conditions: Bz-ol 0.1026 $\mathrm{mol\,l^{-1}}$, 1 g catalyst, 100 ml solvent, $T = 100$ °C, $P_{\mathrm{air}} = 10$ bar.

additional oxygen groups for cationic exchange. As shown by Boehm titration (Table 1), carboxylic, lactonic and phenolic groups were created which could be used as nucleating sites and would favour the dispersion of Pt [38]. Some publications highlighted the role of oxygen surface groups on the platinum dispersion and in particular the possible harmful effect of carboxylic groups whose thermal stability is low [39]. The thermal treatment with H_2 may not only involve reduction of the metallic precursor $\mathrm{Pt(NH_3)_4Cl_2}$, but also the decomposition of the thermally unstable groups acting as anchoring centres and, consequently, the sintering and migration of platinum atoms [40,41]. It is also suggested a particular role of phenolic groups in getting high dispersed metallic particles after cationic exchange [42,43].

Therefore, support $\mathrm{C_{39Cox}}$ was heated under a flow of argon at 500 °C to afford $\mathrm{C_{39Cox/Ar}}$. This treatment should selectively eliminate the thermally unstable carboxylic groups and preserve the more stable phenolic groups. As shown in Table 1, carboxylic groups decreased from 0.50 to 0.09 $\mathrm{mmol\,g^{-1}}$, whilst the amount of phenolic and lactonic groups remained the same. The two carbons were used to prepare platinum catalysts from a solution of $\mathrm{Pt(NH_3)_4Cl_2}$ with nominal 3.5 wt.% of Pt. The characteristics of the resulting catalysts and their performances in dioxane/alkaline aqueous solution pH_i 9.3 50/50 are given in Table 4; typical TEM images of these catalysts are shown in Fig. 2.

The dispersion of $2.7\%\mathrm{Pt_{ex}/C_{39Cox/Ar}}$ measured by CO chemisorption was slightly improved compared to $3.5\%\mathrm{Pt_{ex}/C_{39Cox}}$ (from 5% to 15%) and the particle sizes measured by TEM were smaller (mean particle size 4 nm instead of 6 nm). The initial reaction rate was doubled and the benzoic yield after 23 h of reaction increased from 20% to 66%. Although oxygen surface groups may have a positive effect on the metal dispersion, the presence of nitrogen in this type of carbon (6 wt.%) may also have an effect on the dispersion.

Further improvement of the catalyst activity was obtained by a pre-decomposition of the anchored platinum complex under air, before the reduction step. Indeed, it was shown that in some cases, the decomposition of the complex under an inert gas avoids the sintering of the metal [44,45]. Thus, catalysts $3.3\%\mathrm{Pt_{ex}/C_{39ox}}$/calc and $2.7\%\mathrm{Pt_{ex}/C_{39Cox/Ar}}$/calc prepared by calcinations at 300 °C under air after the exchange step and then reduced in hydrogen gas, with dispersions of 19% and 24%, respectively and a mean particle size of 3.2 and 2.7 nm, respectively (Fig. 2), yielded benzoic acid in 95% yield after 23 h of reaction.

The different treatments improved substantially the dispersion and the catalytic performances of the exchanged catalyst, but, in any case, $2\%\mathrm{Pt_{imp}/C_{38C}}$ showed the highest activity. The latter catalyst was used in subsequent studies.

3.4. Oxidation of various alcohols to the corresponding aldehydes or acids

Oxidation of various alcohols was carried out in either dioxane or dioxane/water mixtures at 100 °C or 10 bar to test the effectiveness and scope of the catalyst. The substituting groups of benzyl alcohols were electron-donating or electron-withdrawing groups. The results are given in Table 5 for substituted benzyl alcohols and in Table 6 for thiophene- and pyridinemethanol compounds.

For most of the substituted benzyl alcohols, high conversion was achieved and the corresponding benzaldehydes or benzoic acids could be obtained with high selectivity, whether the reaction was run in dioxane or dioxane/water (eventually dioxane/aqueous alkaline solution) 50/50 vol.%. As an

Table 4
Oxidation of benzyl alcohol in dioxane/water 50/50 vol.% in the presence of platinum catalysts prepared by cationic exchange of $\mathrm{C_{39Cox}}$

Catalyst	Dispersion (%)	Mean diameter (nm)	Initial rate of Bz-ol conversion ($\mathrm{mol\,h^{-1}\,mol_{Pt}^{-1}}$)	Yield in Bz-oic after 23 h (%)
$3.5\%\mathrm{Pt_{ex}/C_{39Cox}}$	5	6.0	25	20
$2.7\%\mathrm{Pt_{ex}/C_{39ox/Ar}}$	15	4.0	57	66
$3.3\%\mathrm{Pt_{ex}/C_{39Cox}}$/calc	19	3.2	58	95
$2.7\%\mathrm{Pt_{ex}/C_{39Cox/Ar}}$/calc	24	2.7	57	95

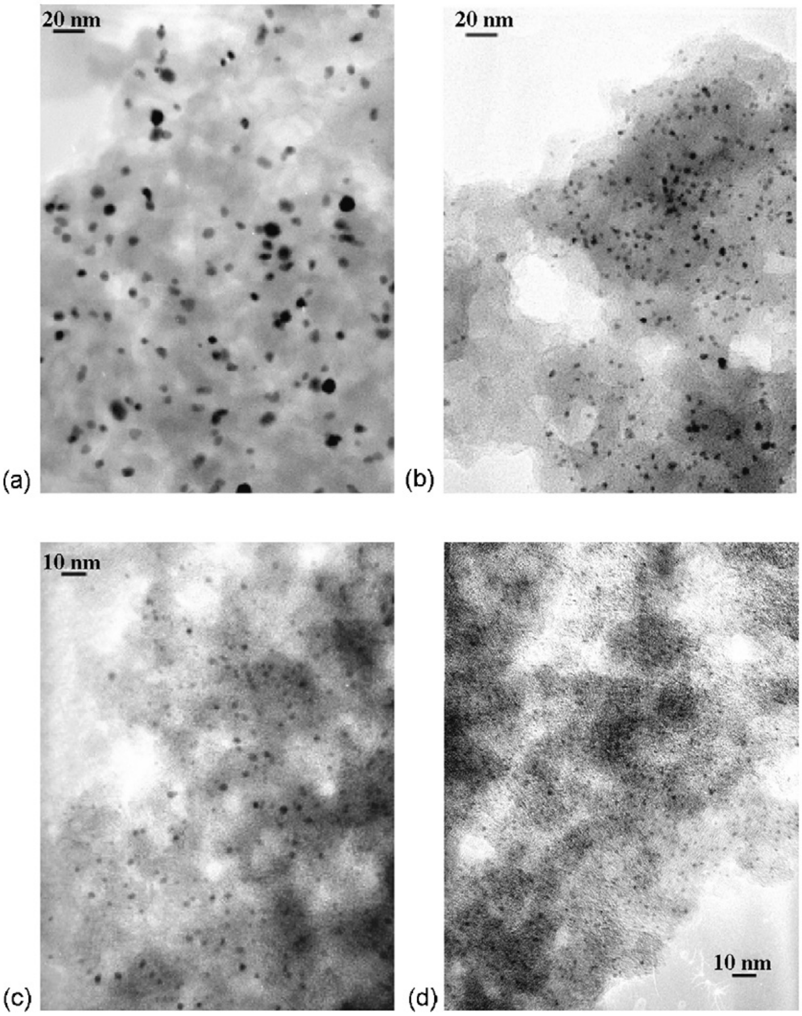


Fig. 2. TEM images of: (a) 3.5%Pt_{ex}/C_{39Cox}, (b) 2.7%Pt_{ex}/$C_{39Cox/Ar}$, (c) 3.3%Pt_{ex}/C_{39Cox}/calc, and (d) 2.7%Pt_{ex}/C39$C_{ox/Ar}$/calc.

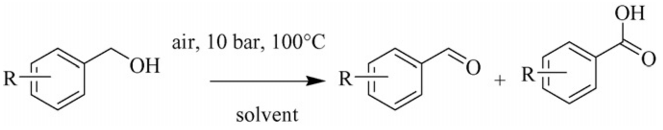
example, the use of dioxane for 2-methylbenzyl alcohol afforded the aldehyde quantitatively after 6 h of reaction. Using a small amount of water (10%) greatly accelerated the reaction; a quantitative yield of aldehyde was obtained within less than 1 h. However, using a dioxane/water 50/50 vol.% mixture, 2-methylbenzyl alcohol was totally converted to the acid. Similarly, 2-nitrobenzyl alcohol afforded the aldehyde or the acid in very good yield. 2-Nitrobenzylaldehyde and 2-nitrobenzoic acid were isolated with excellent yields by simple filtration of the reaction mixture followed by concentration under reduced pressure.

Only a limited number of substituted benzyl alcohols tested displayed a different behaviour in these solvents. This is the case of 4-bromobenzyl acohol. When dioxane was used as solvent, 4-bromobenzaldehyde was rapidly oxidized to the corresponding acid before the total conversion of the alcohol, so that after 6 h of reaction a mixture of 14% aldehyde and 86% acid was obtained at total conversion. Under the same reaction conditions (solvent dioxane, 100 °C, 10 bar air), a ruthenium catalyst, prepared by impregnation with an aqueous solution of $RuCl_3$ of a similar support C_{40C}, was able to achieve high selectivity in 4-bromobenzaldehyde, as shown in Fig. 3. On the other hand, 4-hydroxybenzyl alcohol was very selectively oxidized to the corresponding aldehyde in the presence of platinum in all solvents, even in dioxane/alkaline aqueous solution pH_i 9.3 50/50 vol.%.

The ability of the platinum catalyst to be recycled was examined with benzyl alcohol and 2-methylbenzyl alcohol in dioxane or 90/10 vol.% dioxane/water. The catalyst was recycled through three consecutive runs and the aldehyde was quantitatively produced at the same rate.

The protocol was applied to heterocyclic alcohols including 2-thiophenemethanol and to pyridinemethanol compounds. The results are shown in Table 6. The 2%Pt_{imp}/C_{38C} catalyst showed high catalytic activity for most of these compounds. For example, 2-thiophenemethanol was easily oxidized to give the corresponding aldehyde in quantitative yields in dioxane. Addition of 30 vol.% water greatly accelerated the reaction, so that after 3 h of reaction, a total conversion to the aldehyde was obtained. The transformation of the aldehyde to the acid occurred under alkaline conditions and only acid was formed in dioxane/alkaline aqueous solution after 20 h. Under these reaction conditions, 2- and 4-pyridinemethanol showed lower reactivity in dioxane: no conversion or only 30% conversion could be measured after 16 h,

Table 5
Oxidation of substituted benzyl alcohols using 3%Pt_{imp}/C_{38C} catalyst



R	Solvent	Time (h)	Conversion (%)	Selectivity to the aldehyde (%)	Selectivity to the acid (%)
2-Me	[a]	6	>99	>99	
	90/10[b]	0.7	>99	>99	
	[c]	<16	>99		>99
4-Me	[a]	7	>99	>99	
	50/50[b]	<16	>99		>99[d]
4-iPr	[a]	2	>99	92	
	50/50[b]	<16	>99		95
4-Cl	[a]	3	>99	92	
	50/50[b]	7	>99		>99
4-Br	[a]	6	>99	14	86
4-OMe	[a]	3	>99	>99	
	50/50[b]	<16	>99		>99[e]
4-OH	[a]	<16	90	>99[f]	
	50/50[b]	16	>99	>99	
	[c]	16	>99	>99	
4-NO_2	[a]	<16	>99	>99[g]	
	50/50[b]	4	>99		>99[h]
2-Phenyl	[a]	20	>99	>99	
	50/50[b]	16	>99	50	50
	[c]	8	>99	50	50
4-Phenyl	[a]	16	70	>99	
	50/50[b]	16	>99		>99[i]

Reaction conditions: 50 mmol l^{-1} alcohol, 100 ml solvent, 1 g catalyst, 100 °C, 20 bar air.

[a] Solvent dioxane.
[b] Solvent dioxane/water (*x*/*y*) vol.%.
[c] Solvent dioxane/aqueous solution pH_i 9.3 50/50 vol.%.
[d] Isolated yield 84%.
[e] Isolated yield 80%
[f] Isolated yield 79%.
[g] Isolated yield 88%.
[h] Isolated yield 97%.
[i] Isolated yield 76%.

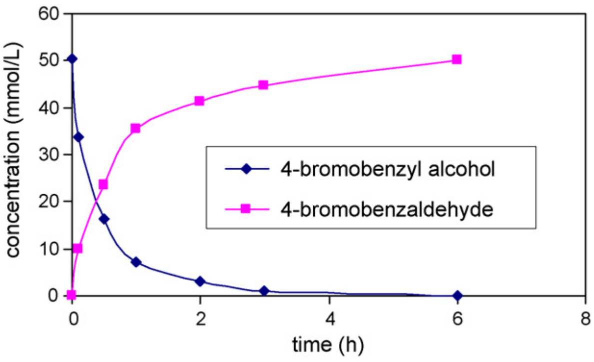


Fig. 3. Oxidation of 4-bromobenzyl alcohol in dioxane in the presence of 3%Ru/C_{40C}. Reaction conditions: 50 mmol l^{-1} alcohol, 100 ml solvent, 1 g catalyst, 100 °C, 20 bar air.

respectively, but, interestingly, the aldehyde was selectively formed. THF was identified as the best solvent, and the yields to the corresponding pyridinecarboxaldehydes were slightly improved. 2- and 4-pyridinemethanol are readily soluble in water and were readily transformed to the corresponding acids with isolated yields of 80% and 77%, respectively. In the cases of substituted 2-pyridinemethanol compounds, the corresponding aldehydes could be obtained in high yields in either dioxane or dioxane/water mixture containing a small amount of water (20 vol.%). The use of dioxane/water 50/50 vol.% afforded the corresponding acids with high yields.

We have also studied the oxidation of other primary alcohols, such as imidazole alcohol (5-formylimidazole derivatives are useful as intermediates for diuretics and hypertensives), uridine (for the synthesis of nucleosides analogues containing a uridine base) or protected aminoalcohols (Fig. 4).

4-Methyl-5-imidazolemethanol hydrochloride was oxidized in the presence of 2%Pt_{imp}/C_{38C}; the reaction rate was found critically dependent on the pH. Whereas the reaction proceeded sluggishly under acidic conditions in water or methanol at 100 °C

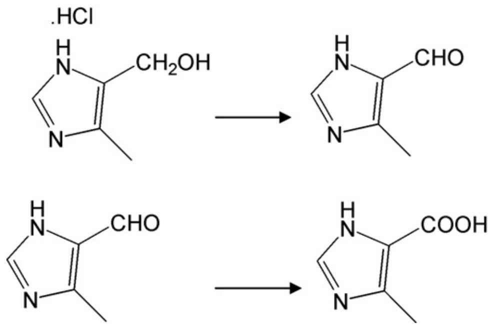


Fig. 4. Oxidation of 4-methyl-5-imidazolemethanol hydrochloride and of 1-methyl-2-imidazolecarboxaldehyde.

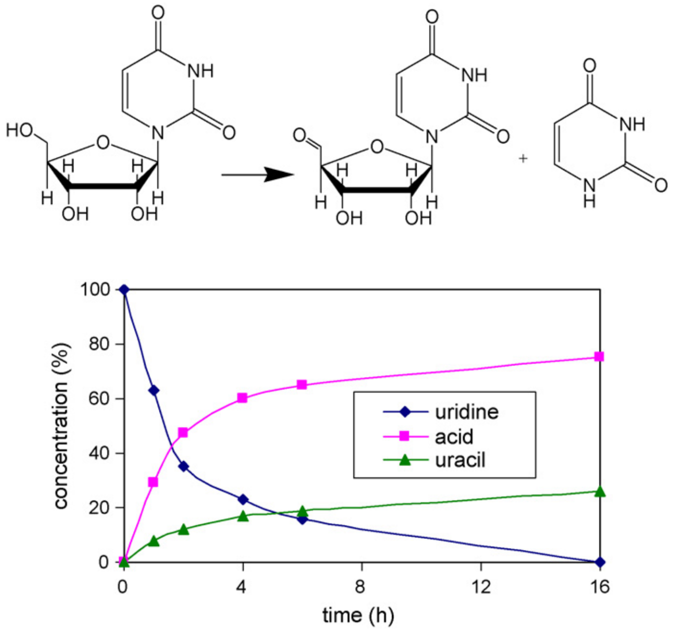
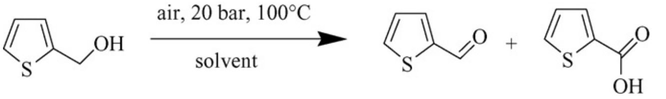
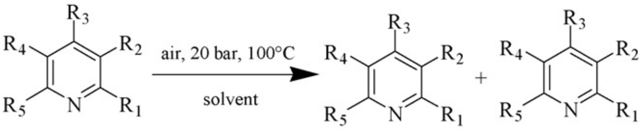


Fig. 5. Oxidation of uridine. Reaction conditions: 30 mmol l^{-1} alcohol, 15 ml solvent, 0.15 g 2%Pt_{imp}/C_{35C}, 100 °C, 20 bar air.

Table 6
Oxidation of heteroaromatic alcohols in the presence of 3%Pt_{imp}/C_{38C} catalyst

Solvent	Time (h)	Conversion (%)	Selectivity to the aldehyde (%)	Selectivity to the acid (%)
				
Dioxane	21	>99	>99	
Dioxane/water 70/30	3	>99	>99	
Dioxane/alkaline aqueous solution pH_i 9.3	20	>99		>99

Substrate	Solvent	Conversion after 16 h (%)	Selectivity to the aldehyde (%)	Selectivity to the acid (%)
				
$R_1 = CH_2OH$, $R_2 = R_3 = R_4 = R_5 = H$	Dioxane[a]	0	>99	
	THF[a]	20	>99	
	Water[a]	>99		>99[b]
$R_1 = R_2 = R_4 = R_5 = H$, $R_3 = CH_2OH$	Dioxane[a]	30	>99	
	THF[a]	46	>99	
	Water[a]	>99		>99[c]
$R_1 = CH_2OH$, $R_2 = OH$, $R_3 = R_4 = H$, $R_5 = Me$	Dioxane[d]	>99	>99[b]	
	Dioxane/water 50/50[d]	>99		>99[e]
$R_1 = CH_2OH$, $R_2 = R_4 = Me$, $R_3 = OMe$, $R_5 = H$	Dioxane[d]	40	>99	
	Dioxane/water 80/20[d]	88	>99	
	Dioxane/water 50/50[d]	>99	17	83[f]

[a] Reaction conditions: 50 mmol l^{-1} alcohol, 100 ml solvent, 1 g catalyst, 100 °C, 20 bar air.
[b] Isolated yield 80%.
[c] Isolated yield 77%.
[d] Reaction conditions: 50 mmol l^{-1} alcohol, 15 ml solvent, 0.15 g catalyst, 100 °C, 20 bar air.
[e] Isolated yield 84%.
[f] Isolated yield 70%.

and 20 bar air, the reaction worked well with initial addition of sodium hydroxide to neutralize the acid. The oxidation of 50 mmol l^{-1} of 4-methyl-5-imidazole-4-carboxaldehyde in an aqueous solution of sodium hydroxide (0.05 M) afforded the corresponding formyl derivative with high selectivity, as observed by ^1H NMR. The acid could not be obtained with an increased concentration of sodium hydroxide. However, in the experiment starting from 1-methyl-2-imidazolecarboxaldehyde, this aldehyde was converted in water with 25–36% conversion to the acid after 17 h of reaction. In the case of uridine, the corresponding acid was obtained with 75% selectivity at 100 °C in 0.05 M NaOH aqueous solution, but 25% of uracil was formed by hydrogenolysis (Fig. 5). *N*,*N*-Dimethylethanolamine was totally converted to the aminoaldehyde after 5 h of reaction in dioxane at 70 °C. The increase in the reaction temperature resulted in the formation of side products.

4. Conclusions

In summary, Pt/C catalysts can be successfully used under mild conditions for the oxidation with air of primary alcohols to the corresponding aldehydes or acids. Though the best conditions and the maximum rates obtainable for each individual alcohol were not optimized, the oxidation protocol was found useful in the oxidation of various types of alcohols. Generally, the alcohol was oxidized to the corresponding aldehyde in dioxane with negligible overoxidation to the acid, whereas the acid was obtained in dioxane/aqueous system mixtures. The addition of sodium hydroxide can promote the formation of the acid. Reaction selectivity was over 99% in most cases. Selectivity of the oxidation of benzyl alcohol to the acid was very dependent on the catalyst preparation and the activation treatment of the carbon used. Carbon-supported ruthenium catalysts have a lower activity, but give for some compounds a high selectivity to the aldehyde.

Selective oxidation with air of alcohols to either aldehydes or acid in the presence of a noble metal catalyst, is of simple work-up procedure, shows a wide applicability to various alcohols and is an attractive, environmental friendly process.

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