Carbon-Supported Platinum Catalysts: Influence of Activation Treatment of a Synthetic Carbon Support and of Metal Deposition in the Selective Liquid Phase Oxidation of Alcohols

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Abstract

Oxidations of alcohols into carbonyl functionalities are key reactions in the synthesis of fine chemicals. The need to substitute stoichiometric oxidations (using mineral oxidants) with "green" oxidations using benign oxidizing agents like molecular oxygen or hydrogen peroxide has been often emphasized. Supported noble metal catalysts, *e.g.* Pd/C or Pt/C are known to catalyse the oxidation of alcohols in the presence of molecular oxygen. It was previously reported that benzyl alcohol (Bzol) can be very selectively oxidized to benzaldehyde (Bzal) in dioxane, whereas the use of a 50/50 mixture of dioxane and alkaline aqueous solution yielded benzoic acid (Bzoic) by further oxidation of Bzal. In this work, we examined the effect of the activation treatment of the synthetic carbon and of the method of deposition of the metal on the characteristics of the supported metallic catalyst and its activity in this reaction. The highest dispersion and best catalytic performances were obtained by impregnation with hexachloroplatinic acid of a CO_2 activated carbon.

INTRODUCTION

The selective oxidation of alcohols in liquid phase provides an access to aldehydes, carboxylic acids and ketones. It is a very important transformation in the field of fine chemicals and pharmaceutical intermediates [1]. Many oxidizing reagents have been developed for the oxidations of this type. Especially attractive is the development of air as oxidizing agent [2]. Such a strategy would lessen the use of more costly oxidants such as hydrogen peroxide, but overall this would lessen the use of environmentally unattractive oxidants such as manganese oxide, potassium permanganate, nitric acid, *etc.*, which are traditionally used to perform these oxidations.

Also catalysts made of noble metal supported by carbon material are of considerable interest due to their application in various processes. In particular, heterogeneous Pd/C and Pt/C catalysts are known to catalyse the oxidation of alcohols with oxygen. These catalysts have long been limited to the oxidation of water-soluble substrates such as carbohydrates and their derivatives [3].

These catalysts could also be used in organic solvents to perform the oxidation of alcohols [4]. In this work, attention was focused on Pt-catalysed oxidation of water-insoluble alcohols. We looked in detail how some parameters of the preparation of the catalyst, such as the activation treatment of a synthetic carbon or the effect of the method of metal deposition, may influence the characteristics of the Pt/C catalyst and its catalytic performances. We were interested in the conditions which will afford either the corresponding aldehyde or the acid with high yield using the same platinum

catalyst, starting from benzyl alcohols for instance. Moreover, this catalyst should also be able to oxidize secondary alcohols such as menthol to menthone.

EXPERIMENTAL

The supported metallic catalysts were prepared on a synthetic carbon from MAST Carbon Technology Ltd. The carbon was prepared by carbonisation at 800 °C of a porous polymeric resin prepared from a phenolic resin and hexamethylenetetramine in ethylene glycol. The resulting carbon is mesoporous. In order to increase the surface area and pore volume, the raw sample was then activated by two different conventional "burn-off" techniques with x % burn-off, using either CO_2 at 850 °C (carbon CxC), or air at 450 °C (carbon CxA). The carbons activated under CO_2 were in some cases oxidized with sodium hypochlorite before the platinum exchange and were denoted CxC$_{ox}$.

The catalysts were then prepared on the activated supports by two methods: either by impregnation with an aqueous solution of hexachloroplatinic acid followed by liquid phase formaldehyde reduction (Pt_{imp}/CxC or Pt_{imp}/CxA), or by ion exchange using tetrammino platinum chloride and reduction under hydrogen gas at 300 °C (catalyst Pt_{ex}/CxC$_{ox}$ or Pt_{ex}/CxA). The aqueous solutions of the precursors used for the preparation were in the appropriate concentrations to obtain Pt loadings of 3 mass %. 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.

Liquid phase oxidation experiments were conducted in a 250 ml static autoclave with magnetically driven mechanical stirring, after purging with argon. Samples of the product mixture were taken from the reactor by means of an internal tube connected to a valve. Analysis of the alcohols and oxygenated products was performed by GC with a DB5 type column. A solution of about 100 mmol alcohol in 100 ml solvent was treated in the presence of 1 g of catalyst at 100 °C and 10 bar air.

TABLE 1

Textural characteristics of different samples of carbons obtained from the isotherms of N_2 adsorption at 196 °C and elemental analysis

Carbon	S_{BET}, m^2/g	Pore volume, cm^3/g	N, %	O, %
C	540	0.6		
C40C	1220	1.1	0.6	4.7
C44A	750	0.8	0.57	25.4

RESULTS AND DISCUSSION

Characterization of activated carbons

The carbon particles are regular spherical activated carbons with particle sizes in the range 90−125 mm. Table 1 gives the characterization of the porous texture of the carbons carried out by N_2 adsorption at 196 °C.

Upon activation in CO_2 or air, the specific surface area increased from 540 to 1220 and 750 m^2/g, respectively. Both mesoporosity and microporosity were developed, but the average mesopore size of 18 nm was not changed. The surface chemistry of the different samples was determined by Boehm titration, *i.e.* titration of the acidic oxygen groups with bases of different strengths: $NaHCO_3$ (carboxylic), Na_2CO_3 (carboxylic and lactones) and $NaOH$ (carboxylic, lactones and phenols) (Fig. 1) [5]. Temperature-Programmed Desorption was also used to characterize the surface oxygen groups. The oxygen functionality of carbon C40C was very poor and was only constituted by phenolic compounds. Oxidation with NaOCl introduced lactonic and carboxylic groups, while activation
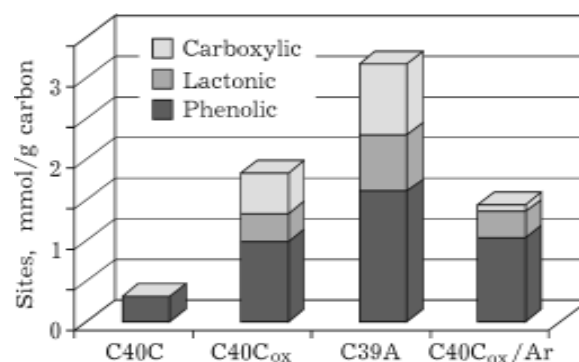

Fig. 1. Characterization of oxygen functional groups by Boehm titration.

in air produced the development of important amounts of oxygen groups.

Oxidation of benzyl alcohol to benzaldehyde or benzoic acid

For the choice of the solvent, the generally accepted mechanism for the oxidation of alcohols on noble metals was considered. It is a stepwise oxidative dehydrogenation involving a first dehydrogenation of the adsorbed alcohol on the metal surface to the aldehyde. Then, if water is present in the system, the aldehyde can react further, to generate the hydrate, a geminol diol, which is further dehydrogenated to produce the carboxylic acid. Whenever the aldehyde is wanted as oxidation product, the solvent chosen was dioxane. On the other hand, when the reaction was operated in dioxane/water 50/50 vol. % and even better in dioxane/aqueous NaOH solution pH ≈ 9.3, the hydration of the aldehyde was favoured. As a result, a high yield in benzoic acid was obtained [6]. However, all catalysts did not behave similarly in this reaction, and different studies were conducted to find the optimum catalyst.

The metallic dispersion, the mean particle size of the different catalysts, and the catalytic performances under standard conditions at 100 °C and 10 bar air in both solvents are given in Table 2.

The influence of the activation treatment of the carbon support on the catalytic performances of the platinum catalysts was studied by comparing 2 % Pt_{imp}/C44A and 2 % Pt_{imp}/C35C, prepared by impregnation of carbons C44A and C35C. The platinum experimental loading for both catalysts prepared by impregnation was 2 % instead of the 3 mass % nominal value. Their dispersion measured by CO chemisorption was comparable (44 and 35 %, respectively), in agreement with the mean particle size determined by TEM (2.5 and 3.0 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 rates, 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) (runs 1 and 2). Further, Fig. 2, *a* and *b* giving the concentration profiles with time in the presence of these two catalysts show that longer reaction times in dioxane did not significantly convert benzaldehyde to benzoic acid in dioxane. When the reaction was performed in the dioxane/alkaline aqueous solution, the conversion of the alcohol to the aldehyde was complete within 2 h in both cases. But after 23 h of reaction, while benzaldehyde was totally oxidised to the acid on 2 % Pt_{imp}/C35C, only 46 % benzoic acid was measured on 2 % Pt_{imp}/C44A (see Table 2, Fig. 2, *c* and *d*). These different results may be attributed to the polar groups on C44A which make the catalyst more hydrophilic. Water formed in the first step may be retained on the metallic

TABLE 2

Oxidation of benzyl alcohol (Bzol) to benzaldehyde (Bzal) or benzoic acid (Bzoic). Reaction conditions: 100 mmol/l, 100 ml solvent, 1 g catalyst, 100 °C, 10 bar air

| Run	Catalyst	Dispersion, %	Mean particle size, nm	Dioxane			Dioxane/NaOH solution	
				Initial rate mol/(h mol_{Pt})	Bzol conversion, %/h	Bzal yield, %/h	Bzol conversion, %/h	Bzoic yield, %/h
1	2 % Pt_{imp}/C44A	44	2.5	51	100/6	95/6	100/2	46/23
2	2 % Pt_{imp}/C35C	35	3.0	63	99/7	98/7	99/2	98/23
3	2.7 % Pt_{ex}/C39A	20	4.2	7	94/23	86/23	100/4	39/23
4	3 % Pt_{ex}/C39C$_{ox}$	5	6.0	7	91/23	85/23	100/4	20/23
5	3 % Pt_{ex}/C39C$_{ox}$/Ar	15	4.0		100/3	66/23		
6	3 % Pt_{ex}/C39C$_{ox}$ calc.	19	3.2		100/3	95/23		
7	3 % Pt_{ex}/C39C$_{ox}$/Ar calc.	24	2.7		100/2	95/23		
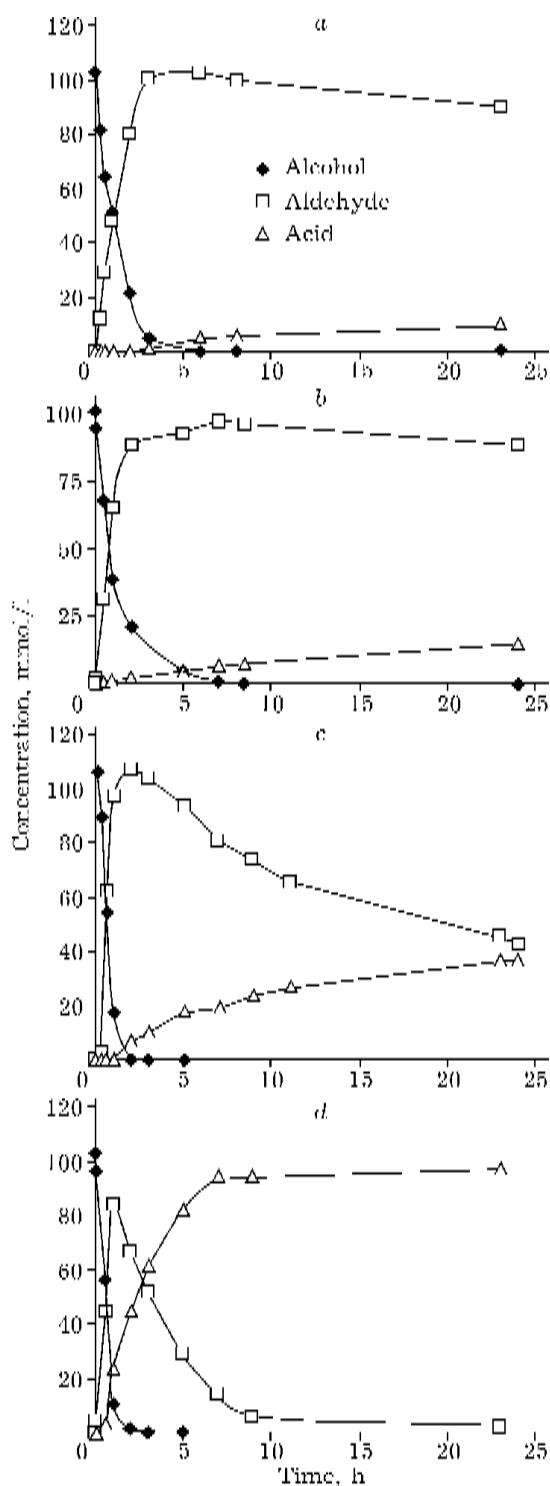
Fig. 2. Catalysts prepared by impregnation with an aqueous solution of chloroplatinic acid: effect of the activation treatment of the carbon in the oxidation of benzyl alcohol in dioxane (*a*) catalyst 2 % Pt_{imp}/C44A and (*b*) catalyst 2 % Pt_{imp}/C35C; and in dioxane/NaOH aqueous solution pH ≥ 9.3 (*c*) catalyst 2 % Pt_{imp}/C44A and (*d*) catalyst 2 % Pt_{imp}/C35C.

surface and act as a poison. In contrast, C35C contains very little polar group and will repel water from the solid.

As concerns the platinum catalysts prepared by cationic exchange on both activated carbons, C39A and $C39C_{ox}$, they showed a low activity in oxidation (see Table 2, runs 3 and 4). In dioxane, conversion was not total after 23 h. In dioxane/alkaline aqueous solution, only 39 and 20 % benzoic acid were formed after 23 h of reaction. The low activity is certainly related to the surprisingly low dispersion, which was only 20 and 5 %, respectively.

As shown by Boehm titration and TPD experiments, carboxylic, lactonic and phenolic groups were created on oxidised supports which could be used as nucleating centres for the generation of highly dispersed metallic crystallites. But it has also been reported that the nature of these oxygen surface groups may have a decisive effect. Thermal decomposition of some of the surface groups (namely carboxylic) may occur at relatively low temperature. Then, when these groups are destroyed, the fixed small particles (or unreduced precursor) will become mobile on the surface and this will favour the agglomeration to larger particles [7, 8]. The less acidic groups (phenol especially) are also thought to be more responsible for the anchorage, and to hinder the sintering of the metal particles during decomposition and reduction of the metal precursor [9, 10]. Therefore, we examined in more detail the influence that the oxygen functional groups may have on the dispersion and catalytic activity in dioxane/aqueous alkaline solution.

Heating $C39C_{ox}$ under Ar (carbon $C39C_{ox}$/Ar) was performed at 500 °C to selectively eliminate carboxylic groups and preserve phenolic groups. This treatment decreased the amount of carboxylic acid groups (as measured by Boehm titration) from 0.5 to less than 0.1 mmol/g, while the amount of phenolic and lactonic groups remained the same. Dispersion of the resulting catalyst prepared by cationic exchange (3 % Pt_{ex}/$C39C_{ox}$/Ar) was slightly improved to 15 % (mean particle size by TEM, 4.0 nm). The reaction rate of oxidation of benzaldehyde in dioxane/alkaline aqueous solution was largely increased and the benzoic acid yield after 23 h of reaction increased from 20 to 66 % (see Table 2, runs 4 and 5).

Pre-decomposition of the complex under air or inert gas before the reduction step in a hydrogen flow could also be beneficial. Thus, catalysts 3 % Pt_{ex}/C39C_{ox} calc. and 3 % Pt_{ex}/C39C_{ox}/Ar calc. were prepared on C39C_{ox} and C39C_{ox}/Ar, by calcinations of the solids in air at 250 °C after the exchange step, and then reduction in hydrogen gas. The dispersions increased to 19 and 24 %, respectively, with a mean particle size of 3.2 and 2.7 nm, respectively. They yielded 95 % benzoic acid after 23 h of reaction (see Table 2, runs 6 and 7). However, these performances remained lower than those of 2 % Pt_{imp}/C35C.

The CO_2 activated carbon was used for further studies. To enhance the stability of the carbon under oxidising conditions, a supplementary treatment of that carbon was performed under inert gas at 2000 °C (C36C-2000HT). This heat treatment eliminated microporosity. The catalyst was prepared by impregnation with hexachloroplatinic acid. The heat treatment of the carbon had a significant effect on the loading capacity, since only 0.9 % Pt could be loaded from the nominal 3 % concentration. Table 3 compares the initial reaction rate per mole of platinum of catalysts prepared on the untreated and heat treated carbons, in the oxidation of benzyl alcohol and in the oxidation of benzaldehyde, in the dioxane/alkaline aqueous solution. The oxidation rate was significantly enhanced for both reactions using the heat treated carbon. These
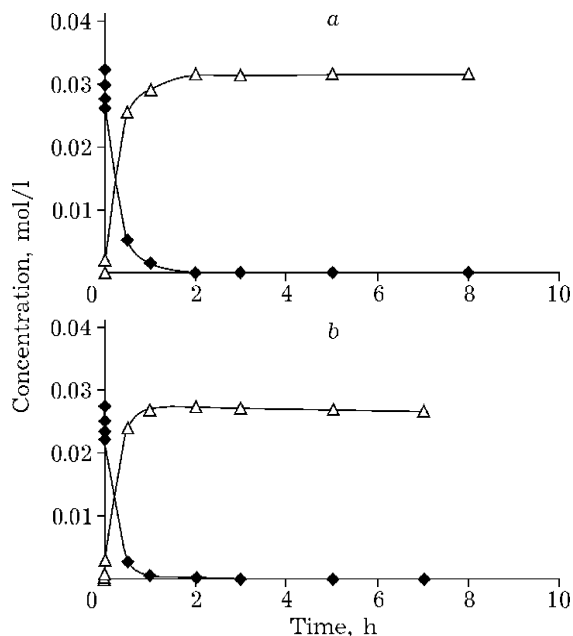

Fig. 3. Oxidation of isoborneol (*a*) and borneol (*b*) in the presence of 3.1 % Pt_{imp}/C39C. Reaction conditions: 32 mmol/l substrate, 100 ml dioxane/water 50/50 vol. %, 100 °C, 10 bar air, 1 g catalyst.

results suggest a better accessibility of the Pt particles in the mesopores than in the micropores. Active sites localised in narrow pores are not easily accessible to bulky organic molecules, especially in liquid phase.

The same catalysts prepared by impregnation or cationic exchange on differently activated carbons were tested in the oxidation of secondary alcohols. Table 4 gives the catalytic results in the oxidation of menthol (32 mmol/l)

TABLE 3

Effect of the heat treatment of a CO_2-activated carbon. Reaction conditions: 100 mol/l substarte, 100 ml solvent: dioxane/NaOH aqueous solution 50/50 vol. %, 100 °C, 10 bar air

Catalyst	Pt loading,	Oxidation, mol/(h mol_{Pt})	
	%	Benzyl alcohol	Benzaldehyde
Pt_{imp}/C35C	2.0	93	19
Pt_{imp}/C35C-2000HT	0.9	184	27

TABLE 4

Oxidation of menthol to menthone. Reaction conditions: menthol (32 mmol/l), 100 ml dioxane/water 20/20 vol. %, 100 °C, 10 bar air, 1 g catalyst

Catalyst	Conversion of menthol, %/time, h	Selectivity to menthone, %
3.1 % Pt_{imp}/C39C	90/8	97
1.6 % Pt_{ex}/C39C_{ox}	0/24	–
3.1 % Pt_{imp}/C39A	16/24	100
2.7 % Pt_{ex}/C39A	5/24	71

to menthone in dioxane/water 20/20 vol. % at 100 °C and 10 bar air.

As observed previously in the oxidation of benzyl alcohol, catalyst 3.1 % Pt_{imp}/C39C prepared by impregnation of a CO_2 activated carbon was the most active in the oxidation of menthol and the selectivity to menthone was very good. Similarly, the two secondary alcohols isoborneol and borneol could be oxidised very selectively to camphor, in dioxane/water 50/50 vol. % (Fig. 3).

CONCLUSIONS

Pt/C can be successfully used under mild conditions for the oxidation of water-insoluble alcohols with air. An important aspect in the catalytic properties of Pt/C is the role of the surface chemistry, which can be modified by treatment with oxidising agents or by applying heat. The oxygen functional groups can act as anchoring centres for the metal precursors favouring the metallic dispersion, but some of them may not be stable under the reduction conditions and may decompose, which favours the sintering of the metal species. The hydrophilicity of the supports, dependent on the presence of oxygen functional groups, may strongly retain water formed and act as a poison. Also, the location of metallic particles on the carbon is an important factor.

The catalytic performances depend both on the activation treatment of the carbon, and on the deposition conditions of the metallic precursors.

Acknowledgements

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