Journal of Catalysis 261 (2009) 23–33

Contents lists available at ScienceDirect

Journal of Catalysis

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Synthesis of very highly dispersed platinum catalysts supported on carbon xerogels by the strong electrostatic adsorption method

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ARTICLE INFO

Article history:
Received 11 September 2008
Revised 24 October 2008
Accepted 27 October 2008
Available online 22 November 2008

Keywords:
Strong electrostatic adsorption
Platinum catalysts
Carbon xerogel
Aqueous sol–gel process
Benzene hydrogenation

ABSTRACT

Highly dispersed Pt/carbon xerogel catalysts are obtained by applying the "strong electrostatic adsorption" (SEA) of hexachloroplatinic acid to carbon xerogels (PZC $= 9.4$) and platinum tetraammine chloride to oxidized carbon xerogels (PZC $= 2.4$). After the reduction step, all these Pt/carbon xerogel catalysts display a very high level of metal dispersion: very small platinum particles (1.1–1.3 nm) are observed by TEM. Pt particle sizes obtained by CO chemisorption are in good agreement with TEM micrographs, which shows that the metal is accessible to reactants. These Pt/carbon xerogel catalysts are very active for the hydrogenation of benzene into cyclohexane.

1. Introduction

For several years, the synthesis of Pt/C fuel cell electrocatalysts has been in a great expansion. The catalytic layer of proton exchange membrane fuel cells (PEMFCs) is indeed a key element to the cell performance; in particular, the carbon pore texture as well as the platinum dispersion and crystalline structure are known to strongly influence the electrode performance [1]. Most of the air/H_2 PEMFC electrodes use platinum catalysts supported on carbon blacks, which are composed of carbon particles (10–30 μm) assembled together as aggregates. The packing of these aggregates, and therefore the pore structure of the catalytic layer, depends on the carbon black nature and on the electrode processing. Typically, at the air-fed cathode, where oxygen, proton and water transports are involved, high potential losses due to diffusion limitations offset the cell performances; this problem is compensated by increasing the metal loading, to the detriment of the cost of such devices. As detailed by Gasteiger et al. [2], the necessary reduction of platinum loading must be led in two ways: (i) improvement of the catalyst activity and efficiency, either by optimizing the metal dispersion or by using appropriate alloys and (ii) improvement of the electrode structure in order to decrease the diffusion-induced potential losses. In the latter field, nanostructured carbons constitute an interesting alternative to carbon blacks.

Recently, carbon aerogels and xerogels were used to replace classical carbon supports in catalysis [3–5] and electrocatalysis [6–9] applications. These materials are obtained either by supercritical drying or evaporative drying of organic gels, followed by pyrolysis [10,11], and their pore texture is fully controllable within a wide range *via* the synthesis variables of the pristine gel. With regard to active carbons or carbon blacks, the advantages of carbon aerogels and xerogels are their high purity and their pore texture flexibility. For example, carbon xerogels were recently used as a Pd and Pd–Ag catalyst supports in order to eliminate diffusional limitations during a gas phase reaction [12]. In previous studies [7,8], PEMFCs cathodes were prepared from Pt catalyst supported on carbon aerogels and xerogels. While carbon blacks are constituted of aggregates connected through van der Waals bonds, carbon aerogel and xerogel powders display monolithic structures at the micrometer scale; as a consequence, the pore texture of a carbon aerogel or xerogel micromonolith remains identical in the catalytic layer of a membrane–electrode assembly [7,8]. These previous works showed that an adequate choice of the carbon pore texture could lead to a significant decrease of the diffusion-induced potential losses. However, the highly loaded (35 wt%) Pt catalysts used in these studies, and prepared by direct deposition of large metal amounts on the support, presented low metal dispersions: up to 60% of the Pt atoms constituted large particles (10–50 nm), which decreased the

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doi:10.1016/j.jcat.2008.10.014

Pt utilization ratio. In addition, the synthesis method was rather long and sophisticated. In order to increase the efficiency of carbon aerogel and xerogel supported Pt catalysts, it is thus necessary to develop a simple procedure to obtain Pt catalysts with relatively high metal loading and optimal dispersion.

Much progress in the preparation of heterogeneous catalyst has been made through the postulate of Brunelle that the adsorption of noble metal complexes onto common oxide supports was essentially coulombic in nature [13]. The hydroxyl (–OH) groups that populate oxide surfaces become protonated and so positively charged below a characteristic pH value, while the same hydroxyl groups become deprotonated and negatively charged above this characteristic pH value. This pH, at which the surface is neutral, is termed the point of zero charge (PZC). Brunelle explained that oxides placed in solutions at pH values below their PZC would adsorb anions such as hexachloroplatinate $[PtCl_6]^{2-}$; at pH values above their PZC, the same support would adsorb cations such as platinum tetraammine $[Pt(NH_3)_4]^{2+}$. A few years ago, Regalbuto et al. studied this adsorption process, beginning with the chloroplatinic acid (H_2PtCl_6 or CPA)/alumina system [14–17]. In this system, anionic chloride ($PtCl_6^{2-}$) and oxy-chloride ($PtCl_5(OH)^{2-}$, $PtCl_4(OH)(H_2O)^-$) complexes adsorb over a positively charged alumina surface in the low pH range. This method, called the “strong electrostatic adsorption” (SEA) method, has also extended to the platinum ammonium chloride ($Pt(NH_3)_4Cl_2$ or PTA)/silica system at high pH [18, 19], where cationic complexes ($Pt(NH_3)_4^{2+}$) adsorb over negatively charged surfaces. The latter two works especially demonstrate the practical consequence that, when strongly adsorbed at the optimal pH, the monolayer of adsorbed coordination complexes retains its high dispersion through the catalyst pretreatment process such as drying and reduction steps. Finally, the SEA method was applied to the activated carbon surfaces because controlled oxidation of a carbon surface at mild or rigorous conditions leads to a lesser or greater amount of oxygen functional groups on the surface [20–23], irreversibly altering the PZC and influencing the adsorption of Pt complexes in a way that is systematic and controllable. In a previous work on activated carbons [24], the highest-PZC active carbons adsorb the largest amount of anions $[PtCl_6]^{2-}$ and the lowest amount of cations $[Pt(NH_3)_4]^{2+}$ while the lowest-PZC active carbons adsorb the lowest amount of anions and the largest amount of cations. Pt uptakes reach a maximum with respect to pH for a given metal precursor and active carbon PZC.

The aim of the present work was to apply the same method to carbon xerogels in order to establish whether or not highly dispersed Pt catalysts can be prepared by optimizing the adsorption pH with regard to both the carbon surface chemistry and the chosen precursor. In this ambit, the PZC of the carbon xerogels, before and after oxidation treatment, was first determined. Then, the influence of PZC alteration on the control of Pt uptake, using both anionic and cationic Pt complexes, was studied. Finally, the impact of the impregnation method on the metal dispersion was checked. The final goal was to develop a simple and effective way to synthesize highly loaded and highly dispersed Pt/carbon materials that could be further used as electrocatalysts in PEM fuel cells.

2. Experimental and methods

2.1. *Synthesis*

2.1.1. *Carbon xerogels synthesis*

Four carbon xerogels with various pore textures were synthesized by the evaporative drying and pyrolysis of resorcinol–formaldehyde gels following a method described in a previous study [25]. Basically, the gel was obtained by polycondensation of resorcinol with formaldehyde in water, with NaOH as basification agent, whose role is to settle the starting pH of the precursor solution. The resorcinol/formaldehyde molar ratio, R/F, was fixed at 0.5 and the dilution ratio, D, i.e. the solvent/(resorcinol + formaldehyde) molar ratio, was chosen to be equal to 5.7. 99 g of resorcinol (Vel, 99%) were first mixed with 188 ml of deionized water in 500 ml vessels under stirring. After dissolution, the pH value was increased close to the chosen starting value with concentrated sodium hydroxide solutions (5 and 2 N). 135 ml of formaldehyde solution (37 wt% in water, stabilized with 10–15 wt% methanol) were added to the mixture, and the pH was then adjusted exactly to the value chosen by the addition of diluted sodium hydroxide solution (0.5 N). In order to cover a wide range of pore textures, the starting pH of the four solutions was adjusted to 5.50, 5.75, 6.00, and 6.25 respectively. The vessels were then sealed and heated up to 343 K for 72 h for gelling and aging. The gels obtained were then dried under vacuum according to the following procedure: the flasks were opened and put into a drying oven at 333 K, then the pressure was progressively decreased down to the minimum value (1200 Pa). This step was performed over 48 h. The samples were then kept at 423 K for 72 additional h. After drying, pyrolysis was performed at 1073 K under flowing nitrogen and following the same temperature program, as described in previous studies [4,25,26]: (i) ramp at 1.7 $K\,min^{-1}$ to 423 K and hold for 15 min; (ii) ramp at 5 $K\,min^{-1}$ to 673 K and hold for 60 min; (iii) ramp at 5 $K\,min^{-1}$ to 1073 K and hold for 120 min; and (iv) cool slowly down to room temperature.

Oxidized carbon xerogels were also prepared by treating the above-obtained carbon materials with nitric acid. 20 g of each carbon xerogel were oxidized in an HNO_3 aqueous solution (5 N) for 48 h at room temperature. Afterwards, oxidized carbon xerogels were washed with deionized water until the pH of the washing solutions reached 4.5. These four samples were dried under vacuum (1200 Pa) at 298 K for 24 h, and then under helium (0.04 $mmol\,s^{-1}$) at 473 K for 1 h to release a great number of micropores. According to Figueiredo et al. [21], no surface oxygen groups are removed at 473 K.

Finally, all unoxidized and oxidized carbon xerogels were crushed and sieved between 100 and 500 μm before their use for the synthesis of Pt/carbon xerogel catalysts by the SEA method.

The four carbon supports are labeled as follows: the letter X (for “xerogel”) is followed by the initial pH of the precursor solution multiplied by 100. For example, X-550 is a carbon xerogel issued from the drying and pyrolysis of a gel prepared at an initial pH of 5.50. In the case of the corresponding oxidized carbon supports, the abbreviation “Ox” follows the names of the initial carbon xerogels (e.g. X-550-Ox).

2.1.2. *Determination of the point of zero charge (PZC) of carbon xerogels*

As explained in the Section 1, when using the SEA method, it is very important to know the PZC of the support, that is the pH value at which the electrical charge density on the support surface is zero. Here, the PZCs of unoxidized and oxidized carbon xerogels were determined by the method of Park and Regalbuto (equilibrium pH at high loading, EpHL) [27]: the porous solid is soaked in water solutions of various starting pHs and after stabilization, the pH is measured again. The PZC of the solid corresponds to a plateau in a plot of the final pH *vs* the initial pH. A critical operating variable in a such system is the total material surface area in solution, i.e. the surface loading, SL (units: $m^2\,l^{-1}$). When comparing samples with different surface areas, the mass of the sample can be adjusted so as to achieve the same SL in each case. In the present study, the SL was chosen to be equal to 10^4 $m^2\,l^{-1}$ for all the carbon xerogels, in line with previous studies [27,28]. Therefore, before measuring the equilibrium pH, the mass of the eight carbon xerogels was adjusted so that $SL = 10^4\ m^2\,l^{-1}$ in 25 ml of water.