Preparation of carbon supported binary Pt–M alloy catalysts (M = first row transition metals) by low/medium temperature methods

Ermete Antolini a,c, Jose R.C. Salgado b, Robson M. da Silva c, Ernesto R. Gonzalez c,*

a Scuola di Scienza dei Materiali, Via 25 Aprile 22, 16016 Cogoleto, Genova, Italy
b Instituto de Química, UnB, C.P. 4478, Brasilia 70919-970, DF, Brazil
c Instituto de Química de São Carlos, USP, C.P. 780, São Carlos 13560-970, SP, Brazil

Received 9 January 2006; received in revised form 8 May 2006; accepted 4 July 2006

Abstract

Carbon supported Pt alloyed with first row transition elements (Pt–M/C) is being used as improved cathode catalyst for low temperature fuel cells. These catalysts have been usually prepared by deposition of the non-precious metal onto pre-formed carbon supported platinum, followed by alloying at temperatures of the order or above 700 °C. As the thermal treatment at high temperature gives rise to an undesired metal particle growth, synthetic methods based on the simultaneous deposition of Pt and M on the carbon substrate, followed by thermal treatment at lower temperature have been developed. In this paper the formation of Pt–M/C by low/intermediate temperature methods is reviewed.

Moreover, to investigate the effect of the conditions used in the synthesis on the Pt:M atomic ratio, the degree of alloying and the particle size, carbon supported Pt–Co electrocatalysts with nominal Pt:Co atomic ratio 75:25 were prepared by a low temperature chemical reduction of the precursors with sodium borohydride at two different temperatures and NaBH₄ concentrations. The physical characterization of these electrocatalysts was performed by energy dispersive X-ray analysis and X-ray diffraction.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Pt-alloys; Nanoparticles; Polymer electrolyte fuel cells; Platinum; Cobalt

1. Introduction

Proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) represent environmentally friendly technologies and are attracting considerable interest as a means of producing electricity by direct electrochemical conversion of hydrogen into water or methanol into water and carbon dioxide, while reducing atmospheric oxygen [1,2]. Platinum has the highest catalytic activity for oxygen reduction of any of the pure metals, so highly dispersed platinum crystallites on a conductive support such as high surface area carbon powders are usually used as electrocatalysts in phosphoric acid fuel cells (PAFC), PEMFC and DMFC air cathodes [3]. However, due to kinetic limitations of the oxygen reduction reaction (ORR) the cathodic overpotential losses amount to 0.3–0.4 V under typical PEMFC operating conditions [3]. Therefore, the search for ORR catalysts more active and less expensive than Pt has resulted in the development of alloy catalysts of platinum with various transition metals [4–10]. Moreover, due to the problem of methanol crossover in DMFCs, developing a sufficiently selective and active electrocatalyst for the DMFC cathode remains one of the key tasks for further progress of this technology. The current direction is to test the activity for the ORR in the presence of methanol of some alloys of the first row transition metals, which present a higher activity for the ORR than platinum in low temperature fuel cells operated on hydrogen [8,11–17].

Carbon supported alloys are commonly prepared starting from the formation of carbon supported platinum (Pt/C) followed by the deposition of the second metal on Pt/C and alloying at high temperatures. Antolini [18] reviewed the characteristics of carbon supported Pt–M alloy catalysts prepared using this method. However, the thermal treatment at temperatures above 700 °C under an inert gas or hydrogen gives rise to an undesired metal particle growth by sintering and coalescence of the platinum particles, which may result in the decrease in Pt mass activity for the ORR since the mass activity of highly dispersed Pt catalysts decreases for particle sizes above 5.5 nm.
The key parameters in the preparation of carbon supported Pt alloys are:

1. The actual Pt:M atomic ratio, which may be different than that expected from the concentrations of the precursors used in the preparation.
2. The amount of M actually alloyed, which can be lower than the total M content in the catalyst.
3. The metal particle size, because the electrocatalytic activity depends on the metal surface area.

In view of the growing of Pt particles when the thermal treatment takes place at temperatures higher than 600 °C [19], an alternative way to prepare carbon supported Pt-based alloys with small particle size is the simultaneous impregnation on the carbon support of Pt and M precursors, followed by reduction at low (<100 °C) or intermediate temperatures (200–500 °C).

This work presents a literature review of the synthesis of carbon supported binary Pt–M alloys (where M represents a first row transition metal) at temperatures lower than 600 °C, recently performed by some research groups engaged in the development of catalysts for low temperature fuel cells. This short review is not intended to be comprehensive, but directed to those methods that have been used recently with good results.

In the case of Pt–Co, the synthesis has been done successfully by impregnation of the carbon support with Pt and Co precursors, followed by reduction with NaBH4, but it has been difficult to obtain catalysts with actual cobalt contents up to 25 at.% Co. Therefore, to aim to integrate the literature data, the preparation of carbon supported Pt–Co alloy catalysts in the atomic ratio Pt:Co 75:25 was experimentally investigated, monitoring the effect of the concentration of the NaBH4 solution and the reaction temperature on Co content, degree of alloying and metal particle size. Both these parameters influence the rate of reduction and have an effect on the rate of nucleation, which determine the number and the size of the primary particles.

2. Experimental

Pt–Co/C electrocatalysts with nominal Pt:Co atomic ratio 75:25 were prepared by impregnating high surface area carbon (Vulcan XC-72, Cabot, 240 m² g⁻¹) with a chloroplatinic acid (H₂PtCl₆·6H₂O, Johnson Matthey) solution and a cobalt hydroxide (Co(OH)₂·6H₂O, Aldrich) solution, using sodium borohydride as the reducing agent. The cobalt hydroxide precursor was soluble in water:methanol 1:1 at pH 2, then the pH was increased to 9 by addition of NH₂OH. The metals were then reduced with a sodium borohydride solution, which was slowly added to the precursors solution under sonication. The concentrations of the NaBH₄ solutions were 0.04 and 0.4 mol L⁻¹. The reduction was carried out at temperatures of 0, 40 and 80 °C.

The atomic ratios of the Pt–Co/C electrocatalysts were determined using the energy dispersive X-ray (EDX) technique coupled to a scanning electron microscopy (LEO Mod. 440 with a silicon detector with Be window and applying 20 keV).

X-ray diffractograms of the catalysts were obtained in a universal diffractometer Carl Zeiss-Jena, URD-6, operating with Cu Kα radiation (λ = 0.15406 nm) generated at 40 kV and 20 mA. Scans were done at 3 ° min⁻¹ for 2θ values between 30° and 100°. In order to estimate the particle size from Scherrer’s equation was used [20]. For this purpose, the (2 2 0) peak of the Pt fcc structure around 2θ = 70° was selected, because it is less affected by the broad band of the carbon support. In order to improve the fitting of the peak, recordings for 2θ values from 60° to 80° were done at 0.02° min⁻¹. The lattice parameters were obtained by refining the unit cell dimensions by the least squares method [21].

3. Literature review

Xiong et al. [22] prepared Pt–M (M = Fe, Co, Ni and Cu) alloy catalysts on a high surface area carbon support by reducing a mixture of chloroplatinic acid and the respective metal salt solution with sodium formate in aqueous medium. Typically, the reduction reaction was carried out at 70 °C. The particle size of the various Pt–M alloys catalysts is reported in Table 1. In the case of Co, the reduction was also carried out by adding first a few drops of sodium borohydride followed by further reduction with sodium formate. The particle size was 3.6 and 4.5 nm, without and with sodium borohydride, respectively. The lattice parameter of the catalysts was not reported. While mild heat treatment at moderate temperature (200 °C) in a flowing mixture of 10% H₂–90% Ar improved the catalytic activity due to a cleaning of the surface oxides, annealing at elevated temperatures (900 °C) reduced the activity of the catalyst due to an increase in particle size.

Water-in-oil microemulsions have been used to synthesise a wide variety of nanoparticles with narrow size distribution and high surface area [23–25]. Xiong and Manthiram [26] synthesised highly dispersed Pt–M (M = Fe and Co) alloy catalysts on a carbon support by the microemulsion method, using sodium bis(2-ethylhexyl) sulfosuccinate as the surfactant, heptane as the oil phase and NaBH₄ as the reducing agent. The synthesis was done at room temperature. For the sake of comparison, the same catalysts were also prepared by a high-temperature method (alloying at 900 °C). The nominal Pt:M atomic ratio was 80:20.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial composition, Pt:M (atomic ratio)</th>
<th>Reducing agent</th>
<th>Composition from EDX</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>–</td>
<td>HCOONa</td>
<td>–</td>
<td>4.8</td>
</tr>
<tr>
<td>Pt–Co/C</td>
<td>17:83 (1:5)</td>
<td>HCOONa</td>
<td>27:73</td>
<td>3.6</td>
</tr>
<tr>
<td>Pt–Co/C</td>
<td>17:83 (1:5)</td>
<td>HCOONa + drop NaBH₄</td>
<td>–</td>
<td>4.5</td>
</tr>
<tr>
<td>Pt–Cu/C</td>
<td>17:83 (1:5)</td>
<td>HCOONa</td>
<td>–</td>
<td>4.7</td>
</tr>
<tr>
<td>Pt–Cu/C</td>
<td>50:50 (1:1)</td>
<td>HCOONa</td>
<td>52:48</td>
<td>4.3</td>
</tr>
<tr>
<td>Pt–Fe/C</td>
<td>50:50 (1:1)</td>
<td>HCOONa</td>
<td>72:28</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt–Ni/C</td>
<td>50:50 (1:1)</td>
<td>HCOONa + drop NaBH₄</td>
<td>–</td>
<td>3.9</td>
</tr>
<tr>
<td>Pt–Ni/C</td>
<td>50:50 (1:1)</td>
<td>HCOONa</td>
<td>73:27</td>
<td>3.7</td>
</tr>
</tbody>
</table>
XRD analysis of the samples prepared by the microemulsion method showed broader peaks compared to those obtained by the high-temperature route, indicating a smaller particle size for the former. The reflections of the Pt–M samples shift to higher angles compared to those of Pt, indicating a contraction of the lattice and alloy formation. However, the shift is more significant for the samples prepared by the high-temperature route than with those prepared by the microemulsion method, suggesting a greater degree of alloy formation in the former case. It is possible that in the samples prepared by the microemulsion method the second metal may not be totally incorporated into the Pt lattice and it may be present as free metal or an oxide. Table 2 compares the EDX composition and the particle size values obtained from the XRD analysis. The Pt–M/C catalysts prepared by the microemulsion method had smaller particle sizes than those prepared by the high-temperature route. With the microemulsion method, the Pt–Co/C sample prepared by a modified procedure (three microemulsion solutions) showed a slightly smaller particle size than the sample prepared using two microemulsion solutions, which could be due to differences in the nucleation and growth rates in the two procedures. Regarding the EDX analysis, while the Pt content in the samples prepared by the high-temperature procedure is close to the expected nominal value, it is lower than the nominal value for the samples prepared by the microemulsion method. The discrepancy is particularly large in the case of the modified microemulsion procedure. According to the authors, the lower Pt content values could be due to the difficulty of effectively reducing the metal ions in the microemulsions since the nucleation and growth processes in the microemulsions are very different from those in the bulk [27], with the consequent loss of metal ions or smaller particles in the filtrate.

Deivaraj et al. [28] synthesised carbon supported Pt–Ni in the Pt: Ni atomic ratio 1:1 by hydrazine reduction of Pt and Ni precursors under different conditions, namely by heating at 60 ◦C, by prolonged reaction (12 h) at room temperature and by microwave assisted reduction. The particle sizes of Pt–Ni prepared by microwave assisted reduction was the lowest, in the range 2.9–5.6 nm, while the particle size of Pt–Ni prepared by thermal treatment at 60 ◦C and by prolonged reaction at room temperature were in the ranges 12.5–50 and 13–25 nm, respectively.

The polyl synthesis method showed to be a very efficient way to prepare nanosized clusters of noble metals or noble metal alloys with transition metals [29–31], and Zhou et al. [32,33] prepared carbon supported Pt, Pt–Ru, Pt–Pd, Pt–W and Pt–Sn binary electrocatalysts with sharp particle size distributions. Using this synthetic method, the same research group prepared a carbon supported Pt–Fe alloy catalyst [14], which was then reduced at moderated temperature (300 ◦C) under hydrogen atmosphere, thus avoiding reduction procedures at high temperatures. For comparison, a high-temperature reduced Pt–Fe/C sample (Pt–Fe/C900) and Pt–Fe/C900B (Fe deposited on pre-formed Pt/C, followed by thermal treatment at 900 ◦C) were also prepared. H2PtCl6 and FeCl3 solutions were mixed well and added to a carbon/ethylene glycol suspension (Pt metal loading 20 wt.%, Pt:Fe atomic ratio 3:1) under mechanically stirred conditions. One mole per litre of NaOH (in ethylene glycol solution) was added to adjust the pH of the solution to about 11 and the temperature was increased to 130 ◦C and maintained for 3 h. After filtration, washing and drying the Pt–Fe/C300 and Pt–Fe/C900 catalysts were obtained by heat treatment at 300 and 900 ◦C under H2/Ar, respectively. The EDX compositions, the lattice parameter and the metal particle size of the catalysts prepared by the polyl method are shown in Table 3. The Pt–Fe atomic ratio of Pt–Fe/C300 was 93:7, which is smaller than that of the Pt–Fe/C900B catalyst (79:21). According to the authors, this may be attributed to the modified polyl synthesis method, in which Fe may not be reduced completely under the adopted experimental conditions. Considering that the lattice parameter was found to be 0.3924 nm for pure platinum and 0.3865 nm for a Pt3Fe alloy [34], from the values of the lattice parameters in Table 3 it can be concluded that Pt–Fe/C prepared with the polyl method is poorly alloyed both after thermal treatment at 300 and 900 ◦C. The Pt–Fe/C900B sample showed a higher degree of alloying, while he mean particle size of the Pt–Fe/C300 catalyst was smaller than those of the other two Pt–Fe catalysts.

A different way to prepare unsupported nanosized Pt-based alloys is the use of organometallic compounds as precursors. By thermal decomposition or by the reduction of organometallic precursors, small nanoparticles of metal or alloy with narrow size distribution can be obtained. Using organometallic precursors,
Sun et al. [35] obtained Pt–Co nanoparticles of about 2 nm. In the same way, nearly monodisperse Pt–Co [36], Pt–Fe [37] and Pt–Mn [38] nanoparticles were prepared by the decomposition of organic precursors. Among the various organometallic precursors used, metal–carbonyl complexes are employed to obtain carbon supported metal or alloy catalysts. By the reduction of Pt and Ru carbonyl precursors, Nasher et al. [39] and Hills et al. [40] prepared carbon supported bimetallic Pt–Ru alloys, while by decomposition of Pt and Ru carbonyls in organic solvents Dickinson et al. [41] also obtained carbon supported Pt–Ru alloys. In all cases, the Pt–Ru catalysts presented small particle size and a narrow size distribution. Recently, Manzo-Robledo et al. [42] prepared carbon supported Pt–Sn catalysts through the carbonyl chemical route. On these bases, Yang et al. used this method to prepare carbon supported Pt–Cr [43] and Pt–Ni [44]. In the case of Pt–Ni/C, Pt and Ni carbonyl complexes were synthesised simultaneously using methanol as solvent through the reaction of Pt and Ni salts with CO at about 55 °C for 24 h. After the synthesis of Pt–Ni carbonyl complexes, Vulcan XC-72 carbon was added to the mixture under N2 gas flow and stirred at about 55 °C for more than 6 h. Subsequently, the solvent was removed and the catalyst powder was subjected to heat treatment at different temperatures under nitrogen and hydrogen, respectively. The alloying temperature under hydrogen ranged from 200 to 500 °C. In the case of Pt–Cr/C, instead, Pt carbonyl and CrCl3 were mixed with the carbon powder, and then thermally treated at 500 °C under nitrogen for 1 h and under hydrogen for 3 h. The total metal loading of all the carbon supported catalysts was about 20 wt.%. The EDX composition of all the catalysts was very close to the nominal value. According to the authors, the nearly linear relationship between the lattice parameter and EDX composition analysis again attests that Cr and Ni are completely alloyed with Pt. The dependence of the lattice parameters of Pt–Cr and Pt–Ni on the EDX composition is shown in Fig. 1, from the data reported in Refs. [43,44]. In the same way, Fig. 2 shows the metal particle size from TEM as a function of the EDX composition. For both Pt–Cr and Pt–Ni the metal particle size decreases with increasing the content of non-precious metal in the alloy. The alloying temperature (200–500 °C) for the formation of Pt–Cr and Pt–Ni alloys via the carbonyl route is much lower than that of previously reported results (700–1200 °C) [18]. Such a lower temperature could be favourable for the formation of carbon supported alloy nanoparticles with small particle size and narrow size distribution, and thus with an homogeneous dispersion. Using the same route, Yang et al. prepared also Pt–Cr [45] and Pt–Ni [46] with 40 wt.% metal loading. Compared with the values for Pt–Cr and Pt–Ni alloy catalysts with 20 wt.% loading, the lattice parameters were very close while the mean particle size showed only a slight increase.

Another way to prepare carbon supported Pt–M alloy catalysts is based on the reduction of the precursors with formic acid at room temperature. Such a method was developed for the preparation of Pt/C [47] and consists in the treatment of carbon powder with formic acid before impregnation with the Pt precursor. The formic acid treated carbon reduces Pt(IV) on its surface. This method produced good results for the preparation of Pt/C. In a work comparing different preparation methods of carbon supported platinum, the material obtained by the formic acid method presented the best performance [48]. Also, carbon supported Pt–Ru [49], Pt–Mo [50] and Pt–Sn [51] were successfully prepared using this method. On this basis, Salgado et al. [52] prepared carbon supported Pt–Co electrocatalysts in the Pt:Co atomic ratios 70:30 and 60:40 through the formic acid route. Instead of a supported alloy, EDX and XRD measurements indicated the formation of supported bimetallic materials, but in this case the two metals were present on the same support and were not alloyed. Indeed, the reducing power of the formic acid is not strong enough to allow the formation of Pt–Co crystallites. Following thermal treatment at 900 °C of these electrocatalysts in a reducing atmosphere, the secondary Pt reflections in the XRD pattern were shifted to higher angles indicating partial alloy formation.

Unsupported nanoscale Pt–Ni [53] and carbon supported Pt [48] and Pt–Ru [54] were successfully prepared by reduction.
of the metal precursors with borohydride at low temperature. On this basis, carbon supported Pt–Co [55,56] Pt–Ni [57] and Pt–Cr [58] alloy electrocatalysts were prepared by impregnating high surface area carbon with Pt and M precursors, followed by the reduction of the precursors with NaBH₄. As shown in Table 4, the EDX composition of Pt–Co and Pt–Cr was lower than the nominal composition, while in the case of Pt–Ni a good agreement between the EDX and nominal compositions was observed. The metal particle size was in the range 3.8–4.8 nm. It has to be remarked that, independently of the EDX composition, the actual composition of the alloy, that is considering only the amount effectively alloyed, was around 92:8. As a consequence, for low M content (10–15 at.% of M) a high degree of alloying was attained, while the degree of alloying was found to be low for the catalyst with high M content (30 at.% of M). The HRTEM image of the Pt–Co/C catalyst prepared by the borohydride method having a Pt:Co EDX composition of 85:15, is shown in Fig. 3, and reveals the asymmetric faceted shape, typically cubooctahedral, of Pt–Co particles [55]. Combined HRTEM/EDX analysis of the sample indicated a Pt:Co atomic ratio of 91:9 for the alloy particle.

Bonnemann et al. [59,60] developed a colloidal method to prepare unsupported and supported metals and alloys. Metal salts of Groups 6–11 metals stabilized by tetraalkylammonium halides with K[BE₃H]. Mono- and bimetallic organosols of Groups 6–11 metals stabilized by tetraalkylammonium halides may be formed either by the reduction of the metal salts using NR₄ hydrotriorganoborates or conventional agents, e.g. H₂ or HCO₂H, after the pretreatment of the metal salts with NR₄X. The chemical reduction of transition metal salts in the presence of hydrophilic surfactants provides straightforward access to nanostructured mono- and bimetallic hydrosols. Mono- and bimetallic nanoparticles stabilized by lipophilic or hydrophilic surfactants of the cationic, anionic or non-ionic type serve as precursors for heterogeneous metal colloid catalysts. In order to prepare heterogeneous catalysts, the precursors may be adsorbed from aqueous solutions on the supports simply by dipping at ambient temperature. They prepared Pt–Rh and Pt–Pd catalysts supported on charcoal effective for the hydrogenation and oxidation of organic substrates. A comparison of catalytic results and CO chemisorption experiments revealed that the protecting surfactants still cover the nanoparticle surface after adsorption on supports, which markedly improves the lifetime of the catalysts. This method could be used also to prepare carbon supported Pt–M (M = first row transition metals) catalysts for low temperature fuel cells.

Summarizing, Pt–M alloy catalysts have been synthesised both by impregnation of a carbon support with a solution of Pt and M precursors, and by adsorption of Pt and M in colloidal form onto the carbon surface. The reduction of platinum and the base metal following the impregnation or adsorption step has been be carried out by different methods: heating in flowing

### Table 4

<table>
<thead>
<tr>
<th>Catalyst (nominal composition)</th>
<th>Pt:M composition by EDX</th>
<th>Particle size (nm)</th>
<th>Lattice parameter (nm)</th>
<th>Pt:M composition by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–Co/C (75:25) [55]</td>
<td>85:15</td>
<td>3.8</td>
<td>0.3874</td>
<td>91:9</td>
</tr>
<tr>
<td>Pt–Cr/C (75:25) [58]</td>
<td>90:10</td>
<td>4.8</td>
<td>0.3906</td>
<td>90:10</td>
</tr>
<tr>
<td>Pt–Ni/C (90:10) [57]</td>
<td>87:13</td>
<td>4.1</td>
<td>0.3887</td>
<td>92:8</td>
</tr>
<tr>
<td>Pt–Ni/C (70:30) [57]</td>
<td>71:29</td>
<td>4.8</td>
<td>0.3898</td>
<td>94:6</td>
</tr>
</tbody>
</table>

Fig. 3. HRTEM image of the Pt–Co/C catalyst prepared by the borohydride method with a Pt:Co EDX composition of 85:15 [55].
hydrogen in the temperature range 300–500 °C, and chemical reduction with sodium borohydride, sodium formate, hydrazine and formic acid at temperatures lower than 100 °C.

The most promising methods are the microemulsion method, the carbonyl route and the impregnation followed by reduction with NaBH₄. The metal particle size of the catalysts prepared by these methods was in the range 2.3–4.8 nm, smaller than that of the catalysts prepared by alloying at 900 °C, which produces Pt–M particles with sizes in the range 4.5–7.5 nm [6,8,62,63].

For the catalysts obtained by the carbonyl route, the degree of alloying was nearly the same as that of the high-temperature reduced catalysts, while in the case of the catalysts synthesised by the microemulsion method, the alloying was slightly lower than the materials prepared by thermal treatment at high temperature. Finally, regarding the synthesis by reduction with NaBH₄, a high degree of alloying was obtained only for low Pt:M atomic ratio.

With respect to the Pt:M atomic ratio, in some cases the composition of the synthesised material is different than that expected from the preparation conditions. For this reason, carbon supported Pt–Co electrocatalysts were prepared here by the impregnation/NaBH₄ reduction method under different reaction conditions in order to investigate the effect of the concentration of the NaBH₄ solution and the temperature on the characteristics of the resulting Pt–Co/C catalysts.

4. Synthesis of Pt–Co/C (Pt:Co = 75:25) by the borohydride method at different concentrations of NaBH₄ and different temperatures

Table 5 gives the EDX results of Pt–Co particles prepared with two NaBH₄ concentrations and at several reaction temperatures. The metal loadings were in the range 16–20 wt.%. The Pt–Co compositions were characterized by EDX measurements on several different regions of each sample of the carbon supported Pt–Co material. The deviation in the Pt:Co compositions in different regions is ±10%.

At a fixed temperature, the Co content of the catalysts prepared using 0.4 mol L⁻¹ NaBH₄ was always higher than that obtained with 0.04 M NaBH₄. Also, the amount of Co in the samples prepared with 0.4 M NaBH₄ was always higher than the nominal Co content (25 at.%). With 0.04 M NaBH₄, instead, the Pt:Co atomic ratio was lower but closer with respect to the nominal value, except for the sample prepared at 40 °C.

Fig. 4 shows the XRD patterns of the Pt–Co alloy electrocatalysts in the nominal Pt:Co atomic ratio 75:25 prepared by the borohydride method at different temperatures and concentrations of the reducing agent. Carbon supported Pt from E-TEK is also included for comparison. As indicated in Fig. 4, in all the samples only the reflections corresponding to the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), characteristic of the face-centered cubic (fcc) structure of Pt were present. In the binary Pt–Co electrocatalysts these five diffraction peaks were shifted to higher values of 2θ, which is indicative of a contraction
of the lattice, due to alloy formation between Pt and Co. No characteristic peaks of metallic Co or cobalt oxides were detected, but their presence cannot be discarded because they may be present in a small amount or even in an amorphous form. Since there were no superlattice lines in the XRD patterns, it can be concluded that all the alloy catalysts are solid solutions and not intermetallic compounds. The lattice parameters of Pt–Co alloy catalysts, which reflect the formation of the solid solution, are given in Table 5. The values of the lattice parameters are smaller for the Pt–Co materials than for Pt (0.3924 nm), due to the contraction of the lattice due to the partial substitution of Pt by Co in the fcc structure. Indeed, the value of the lattice parameter is related to the amount of Co alloyed, because a smaller lattice parameter corresponds to a higher Co content in the alloy. Surprisingly, notwithstanding the fact that the amount of Co in the catalyst prepared with 0.4 M NaBH4 was higher, the amount of Co alloyed, excluding the sample prepared at 40 °C, was higher for the catalyst prepared with 0.04 M NaBH4. Using also the data of carbon supported Pt–Co obtained by the borohydride method at 25 °C and 0.04 M NaBH4 from Ref. [55], the lattice parameter versus the synthesis temperature was plotted in Fig. 5. In the range 0–40 °C the lattice parameter decreases with increasing synthesis temperature. By increasing the temperature, the rate of reduction of Co3+ ions increases (it has been remarked that the reduction rate of the Co precursor is critical, being lower than that of the Pt precursor), and as a consequence the amount of Co alloyed increases. From the values of the lattice parameters the degree of alloying was calculated according to the method reported in Ref. [64]. As shown in Table 5, for 0.04 M NaBH4 the degree of alloying decreased slightly with increasing reaction temperature (from 50 to 40%). When 0.4 M NaBH4 was used, instead, the degree of alloying at synthesis temperatures of 0 and 80 °C was very low. In these materials most of the Co is in a non-alloyed state. The amount of non-alloyed Co, x_{naCo}, is given by

$$x_{naCo} = (1 - Y_a)x_{Co}$$

where $Y_a$ is the degree of alloying and $x_{Co}$ is the Co atomic fraction in the catalyst. Fig. 6 shows the amount of non-alloyed Co versus synthesis temperature for both concentrations of the reducing agent 0.04 and 0.4 M NaBH4. As can be seen in Fig. 6, the amount of non-alloyed Co for 0.4 M NaBH4 was always higher than that for 0.04 M NaBH4.

The average size of the Pt–Co alloy nanoparticles was estimated by using the Scherrer’s equation, $d = 0.94k_1/B(2) \cos \theta$, where $d$ is the average particle diameter, $k_1$ the wavelength of X-ray radiation (0.154056 nm), $\theta$ the angle of the (2 2 0) peak, and $B(2)$ is the width in radians of the diffraction peak at half height. The obtained average particle sizes of all the catalysts are given in Table 5. As can be seen in Table 5, at the synthesis temperature of 0 °C, the metal particle size decreases with increasing borohydride concentration. In the same way, at fixed NaBH4 concentration the particle size decreases by increasing the temperature from 0 to 40 °C. Using also the data of carbon supported Pt–Co obtained by the borohydride method at 25 °C and 0.04 M NaBH4 from Ref. [55], a linear dependence of the metal particle size on synthesis temperature in the range 0–40 °C was obtained, as shown in Fig. 5. By increasing the concentration of NaBH4 and the synthesis temperature, the rate of metal reduction, and as a consequence the rate of nucleation, increases. As the number of nuclei formed is higher the size of the clusters is smaller.

The anomalous increase of the metal particle size when the synthesis temperature goes from 40 to 80 °C can be explained by considering that at 80 °C in an acid environment dissolution of the smaller particles with re-precipitation of Pt (and not Co) with formation of large particles with low Co content can occur, in agreement with the work of Watanabe et al. [65], which reported that both Pt and Co dissolve out preferentially from small-size alloy particles and Pt re-deposits on the surface of large particles in hot H3PO4.

Summarizing, the catalysts prepared at 40 °C presented the smallest metal particle size and the highest amount of Co alloyed, independently of the NaBH4 concentration. The largest metal particle size and the lowest Co content in the alloy were those of the catalysts prepared at 80 °C for both NaBH4 concentrations.
5. Conclusions

Different methods to prepare carbon supported Pt–M alloys (M = first row transition metal) are described in literature. The microemulsion method, the carbonyl route and the impregnation of Pt and M precursors on the substrate, followed by reduction with NaBH4 are the most promising ways to obtain suitable Pt–M/C electrocatalysts. The metal particle size of the carbon supported alloy catalysts synthesised by these methods is smaller than that obtained by high-temperature methods.

The degree of alloying of catalysts synthesised by low/intermediate temperature methods is related to the preparation method and to the amount of non-precious metal (in the case of the reduction with NaBH4). In the more favourable cases, the degree of alloying is the same or slightly lower than that obtained by alloy formation at high temperatures.

The results of the study of the activity of carbon supported Pt–Co alloy catalysts prepared by reduction with NaBH4 at different concentrations and at different temperatures, can be summarized as follows:

(1) The amount of Co in the catalyst increases with increasing NaBH4 concentration.

(2) In the range 0–40 °C the lattice parameter decreases with increasing synthesis temperature, because of the increase of the degree of alloying. At 80 °C, instead, an increase of the lattice parameter occurs, owing to dissolution of the smaller particles with re-precipitation of Pt and not Co.

(3) The amount of non-alloyed Co increases with increasing NaBH4 concentration.

(4) An anomalous increase of the metal particle size when the synthesis temperature increases from 40 to 80 °C is observed, due to a dissolution/precipitation mechanism.

Acknowledgment

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Proc. 300477/2005-8 for financial assistance to the project.

References