Heat-Treated Fe/N/C Catalysts for O₂ Electroreduction: Are Active Sites Hosted in Micropores?

Frédéric Jaouen,*,† Michel Lefèvre,† Jean-Pol Dodelet,*,† and Mei Cai‡

INRS Énergie, Matériaux et Télécommunications, 1650 Bd Lionel Boulet, Varennes, Québec, Canada, J3X 1S2, and General Motors Research & Development Center, 30500 Mound Road, Warren, Michigan 48092

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Limited availability of platinum is a potential threat to fuel cell commercialization. Since the 1970s, alternative catalysts to the electrochemical reduction of oxygen have been obtained from heat treatment at $T > 600$ °C of carbon with a non-noble metal and a source of nitrogen atoms. However, the process by which the heat treatment activates these materials remains an open question. Here, we report that the activation process of carbon black and iron acetate heat-treated in NH_3 comprises three consecutive steps: (i) incorporation of nitrogen atoms in the carbon, (ii) micropore formation through reaction between carbon and ammonia, and (iii) completion of active sites in the micropores by reaction of iron with ammonia. Step (ii) is the slowest. Moreover, the microporous surface per mass of catalyst controls the macroscopic activity when enough nitrogen atoms are incorporated in the structure of the carbon support. These facts should help in determining the structure of the active sites and in identifying methods to increase the site density of such catalysts.

Introduction

The replacement of platinum by non-noble catalysts for the oxygen reduction reaction in low-temperature fuel cells is desirable.[1] In this prospect, much attention has been paid to catalysts obtained from the heat treatment at 600−1000 °C, in an inert or reductive atmosphere, of a carbon powder together with a transition metal (iron and cobalt) and a nitrogen source.[2,3] The precursors of metal and nitrogen were exclusively metal chelates (one metal atom bound to four nitrogen atoms) until 1989, when Gupta and co-workers[4] synthesized catalysts from the treatment at 800 °C of polyacrylonitrile with Co^{II} or Fe^{II} salts. Separating the nitrogen source from the metal one resulted in a more flexible synthesis route. Following this route, various nitrogen sources have been explored: either solid (pyrrole and phenanthroline[5−9]) or gas (ammonia and acetonitrile[10−14]). This introduction focuses henceforth on catalysts obtained by this synthesis route.

For such catalysts, it is presently known that the active metal ions are in a +2 or +3 oxidation state and interact with pyridinic nitrogen, as shown by X-ray photoelectron spectroscopy.[12] X-ray absorption spectroscopy (XAS)[7−9] revealed that (i) an active metal atom is surrounded by about four nitrogen atoms and (ii) the bond lengths Co−N and Fe−N are 0.190 and 0.196 nm, respectively, compared to 0.194 and 0.204 nm in respective pristine porphyrins.[7,15] Similar results were obtained from XAS on heat-treated metal chelates.[3,15−16] With time-of-flight secondary-ion-mass-spectrometry, the collected ions (catalyst obtained from iron acetate adsorbed on a synthetic carbon and heat-treated in NH_3) were classified into two families: $FeN_xC_y^+$, with $x = 1$, 3, or 4, and $FeN_2C_y^+$, the latter being the tag of superior activity.[13,17] That iron is emitted from the surface with two nitrogen atoms does not, however, preclude a 4-fold coordination, if two other nitrogen atoms remain on the carbon structure.

A weakness of all previous studies on non-noble catalysts originates from the sole examination of catalysts obtained after a unique time of heat treatment (usually 1 or 2 h, preceded by a slow temperature ramp). This weakness has prevented the cogwheels of the heat-treatment activation from being comprehended. This study reports the effect of the time and temperature of heat treatment on the catalytic activity. Both time and temperature are accurately controlled with the know-how of heating a carbon powder from room temperature to, e.g., exactly 900 °C in 1.5 min. Catalysts are obtained from the heat treatment of one carbon black with iron acetate in ammonia. Despite restricting this study to a single carbon black, a sweeping variation in pore structure is obtained, owing to a continuous reaction between carbon and ammonia at high temperature. The rise and fall of the activity with time are mimicked by those of the micropore area.

Experimental Section

Catalyst Synthesis. The carbon black (Sid Richardson Carbon Company) is a furnace black (generalities about furnace blacks can be found in ref 18) in fluffy form, having a BET surface area of 71 m² g⁻¹. Iron acetate is weighed (m_{FeAc}) and dispersed in distilled water. If x is the desired iron content in the C + Fe catalyst (0.2 wt % Fe yields $x = 2 \times 10^{-3}$), then the mass of carbon to add is $m_{FeAc} \cdot t(1 - x)/x$ ($t = 0.3212$ is the mass of iron in iron acetate). Commonly, 550−600 mg of carbon is added and dispersed in 100−120 mL water. The solution is magnetically stirred for 2 h, followed by evaporation of about ³/₄ of the liquid volume on a heating plate, and then the powder is completely dried overnight in an oven (air) at 80 °C. About 500 mg of the resulting powder is ground and placed in a quartz boat (10 cm long, 1 cm wide). The exact initial mass of powder, m_i, is known by allowing for the tare of the quartz boat. A quartz tube (D 3.8 cm, L 120 cm) is installed in a hinged split tube furnace (Thermcraft) with a 40 cm long heating zone. The quartz boat with the powder, as well as a glass rod/interior magnet assembly, is placed in the quartz tube, but outside of the oven.

* To whom correspondence should be addressed. E-mail: dodelet@emt.inrs.ca; jaouen@emt.inrs.ca.

† INRS Énergie, Matériaux et Télécommunications.

‡ General Motors Research & Development Center.

The tube is first purged with argon at 1000 sccm min^{-1} for 20 min. The oven is then switched on and allowed to stabilize at its set temperature for 120 min (see Supporting Information) under argon/hydrogen flows of 1000/100 sccm min^{-1}, respectively. After 100 min of oven stabilization, the argon/hydrogen flow is switched to pure ammonia with a flow rate of 2000 sccm min^{-1}. Twenty minutes later, the boat is pushed by a glass rod/magnet assembly into the middle of the oven by pulling with an outer magnet the glass rod/interior magnet assembly. The boat is pushed in the oven center in three steps of about 30 s each. The 90 s ensures that the temperature sensor of the oven is not perturbed by the cold boat. Once the boat is in the center of the oven, the chronometer is started and the heat treatment is ended by removing the quartz tube from the oven. This takes only a few seconds. The cooling is fast and within 1 min the temperature of the tube's outer surface is close to 100 °C. When the tube has been out of the oven for 10 min, the ammonia flow is replaced by an argon flow for 10 more minutes. The exact mass of powder after the heat treatment, m_f, is known by allowing for the tare of the quartz boat and catalyst powder together, and the quartz boat is scooped out. The weight loss of the carbon during the heat treatment, W, is calculated from $W = 100 \cdot (m_i - m_f)/m_i$. Note that the weight loss W is also a slight function of the size and shape of the quartz boat. A unique boat was used here.

Electrochemical Characterization. The catalytic activity is measured at room temperature in a one-compartment glass cell filled with a solution of sulfuric acid of pH 1, saturated before each measurement by bubbling pure O_2.

An ink of the catalyst is prepared by mechanically and ultrasonically mixing 10 mg of catalytic powder, 95 μL of a 5 wt % Nafion solution (Aldrich), and 350 μL of ethanol for 30–60 min. Seven microliters of the ink are pipetted onto a glassy carbon disk (0.2 cm^2), resulting in a catalyst loading (iron plus carbon black) on the glassy carbon of 0.8 mg cm^{-2}. Cyclic voltammograms with a sweep rate of 10 mV s^{-1} are recorded in the potential range of -0.25 to 0.75 V vs a saturated calomel electrode (SCE), while the counter electrode is a Pt wire. When the electrode is not rotated, in the downward potential scan, a peak of reduction current occurs, owing to O_2 reduction kinetics combined with O_2 diffusion in the electrolyte. The potential at which this peak occurs, V_{pr}, is characteristic of the catalytic activity. The more positive the V_{pr}, the better the activity. A second measure of the catalytic activity is obtained by rotating the electrode at 1500 rpm and correcting the current for double-layer current and limitation by O_2 diffusion in the electrolyte according to the Koutecky–Levich equation. The value of the kinetic current density at a voltage of 0.5 V vs SCE is representative of the activity. These two measures of the activity are reliable and correlated (see Supporting Information). In the article, only the kinetic current density at 0.5 V vs SCE is reported, while activity in terms of V_{pr} is reported in the Supporting Information.

Other Characterizations. X-ray photoelectron spectroscopy was performed using a VG Escalab 200i instrument. The X-ray source is the Al Kα line (1486.6 eV). Narrow scans were performed for the C_{1s} and N_{1s} core levels.

Brunauer–Emmett–Teller (BET) surface area and pore size measurements were determined for the catalysts with a Micromeritics Model 2010 Accelerated Surface Area and Porosimetry system (ASAP). Samples pretreatment was critical for micropore determination. Catalyst samples of 100 mg were degassed at 100 °C under vacuum overnight, followed by 2 h at 200 °C. The samples were tared and placed on the analysis

port. Prior to analysis, the samples were heated to 200 °C for an additional 2 h under vacuum. Adsorption and desorption isotherms were measured at 77 K with N_2 as adsorbate down to relative pressures P/P_o of 5×10^{-7}. The adsorption data were analyzed with the Brunauer–Emmett–Teller theory and, for the pore size distribution, with the nonlocal density functional theory (NLDFT) assuming a slit-pore geometry (Autosorb software from Quantachrome Instruments). The macroporous area was assessed by retrieving from the BET area the micro- and mesoporous areas obtained by the NLDFT analysis.

Analysis of the bulk Fe content of some catalysts was made by neutron activation analysis at the École Polytechnique de Montréal.

Results

An example of a catalyst label is CB/0.2% Fe/900 °C/20 min NH$_3$. CB stands for carbon black; 0.2% is the iron loading (wt %) on the carbon prior to heat treatment; 900 °C is the heat-treatment temperature; 20 min is the heat-treatment duration in NH$_3$.

We first wanted to examine the catalytic activity for the O_2 reduction of catalysts obtained after various times of heat treatment in NH$_3$ for a typical Fe loading (0.2 wt %) and at a typical temperature (950 °C). The fine control of the heat-treatment duration (Experimental Section and Supporting Information) enables one to follow a 2-decade rise in the activity during the first 20 min of heat treatment (Figure 1A, open circles). Full E–log I plots, whereof the kinetic current at 0.5 V vs SCE is derived, are shown in the Supporting Information. The lowest measured activity (0.03 mA mg^{-1}) still lies far above that of the pristine carbon (the latter is too low to be quantified). The activity first rises with time of heat treatment and reaches a maximum after 20–25 min of heat treatment. Then, surprisingly, the activity falls by 4 to 5-fold before reaching a plateau after 40 min. The same study was repeated at 900 and 1000 °C (Figure 1A). The same curve shape reoccurred but on an ever-curtailed time scale as the heat-treatment temperature was raised. Thus, active sites form faster at higher temperature (see Supporting Information for discussion on macroscopic activity, single-site activity, and density).

At this point, we believed that time was required because Fe and/or N would diffuse on the carbon surface before completing a site (even at the shortest times, catalysts have >2 at. % of N, which from our experience is enough to obtain the highest activities seen in Figure 1A). On this premise, the catalyst CB/0.2% Fe/950 °C/5 min NH$_3$ (catalyst 1, activity 0.15 mA mg^{-1}) was given a second heat treatment for 15 min, but in argon (catalyst 2). Thus, catalyst 2 was subjected to a total of 20 min of heat treatment at 950 °C, a time expected to be optimal (Figure 1A). Surprisingly, the activity of catalyst 2 is the same as that of catalyst 1, despite retaining 2 at. % N. For comparison, the catalyst CB/0.2% Fe/950 °C/20 min NH$_3$ has an activity of 2.4 mA mg^{-1}. Clearly, the time of heat treatment is not the key factor. At high temperature, both time and ammonia are required to form many active sites. This directs us to a characteristic of the catalysts not yet spoken of: their weight loss during the heat treatment, W (definition in Experimental Section). Since the catalysts contain >96 wt % C, the weight loss of the catalyst is in practice that of the carbon black. The weight loss is ascribed to carbon forming volatile products with ammonia.[19] The plot of the activity against the weight loss percentage W, instead of time, leads to a stunning result: the three curves of Figure 1A are now superimposed (Figure 1B). Thus, to a given value of weight loss percentage, W_{given} corresponds one activity, regard-

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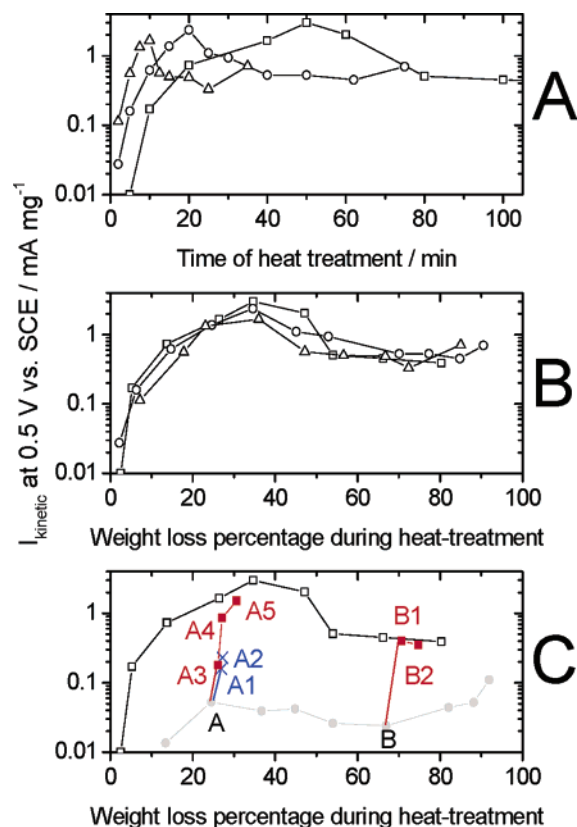
Figure 1. Effect of heat-treatment time and temperature on the activity. Kinetic current of oxygen reduction at 0.5 V vs SCE per mass of catalyst against (A) the time of heat treatment and (B) the weight loss percentage of carbon during heat treatment. Heat treatment in pure NH_3 at 900 °C (□), 950 °C (○), and 1000 °C (△). All with 0.2 wt % Fe initial loading. (C) Two-steps heat treatment: first step is heat-treating the carbon (950 °C) without adding iron (●). Thereafter, adsorbing iron acetate on the heat-treated carbon (point A or B) and the second-step is heat-treating such compounds at 900 °C in either argon (blue **X**) or NH_3 (red ■). *Argon:* Catalyst *A1*: heat-treated carbon A/0.27 wt % Fe/900 °C/5 min argon and *A2*: idem but 12 min argon. *NH_3:* Catalyst *A3*: heat-treated carbon A/0.27 wt % Fe/900 °C/2 min NH_3. *A4*: idem but 5 min NH_3. *A5*: idem but 12 min NH_3. Catalyst *B1*: heat-treated carbon B/0.61 wt % Fe/900 °C/5 min NH_3. Catalyst *B2*: idem but 12 min NH_3. The symbol (□) refers to catalysts as defined in Figure 1A,B.

less of the time and temperature of heat treatment used to obtain W_{given}. This explains why catalyst 2 has the same activity as catalyst 1: Argon does not react with carbon and no weight loss occurred during the second heat treatment.

A brief digression is made here regarding the plateau of activity observed at long times (Figure 1A). Despite a common initial loading of 0.2% Fe (measured to be 0.18 wt % by neutron activation analysis), the catalysts have an actual loading that depends on the percentage of weight loss, W. For example, the Fe content is 0.19% for a catalyst with $W = 15$ wt % loss, 0.53% for a catalyst with $W = 70$ wt % loss, and 1.48% for a catalyst with $W = 90$ wt % loss. It means that while some carbon is volatilized, all of the initial mass of iron remains. The Fe content measured by neutron activation corresponds thus to about 0.2% $\times$ 100/(100 − W). Consequently, past the optimum time, the evolution of the activity per actual mass of iron in the catalysts differs from that of the activity per mass of catalyst (carbon, iron, and nitrogen). The activity per actual mass of iron is equal to the activity per mass of catalyst divided by the actual Fe content per mass of catalyst. Due to increasing Fe content with increasing weight loss, the activity per actual mass of iron constantly decreases with increasing time of heat treatment for $W > 40\%$.
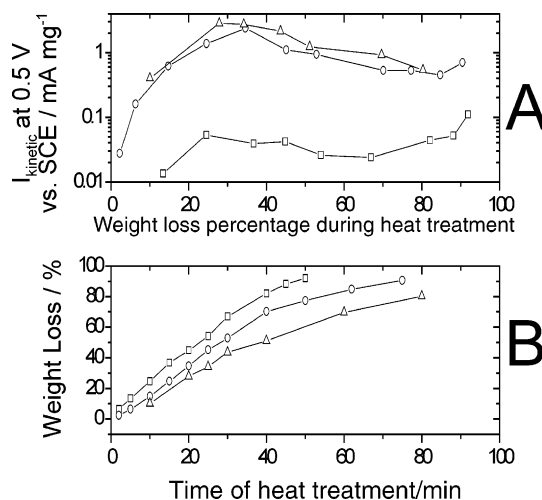
Figure 2. Effect of heat-treatment time and of initial iron loading on the activity. (A) Kinetic current of oxygen reduction at 0.5 V vs SCE against weight loss percentage of carbon during heat treatment. Time is a covert parameter. (B) Weight loss percentage of carbon against time of heat treatment. Initial iron loading 0 (□), 0.2 (○), and 0.4 wt % (△). All heat treatments at 950 °C in pure NH_3.

The above results demonstrate that site formation requires weight loss. Consequently, the weight loss must impart a specific structure or composition to the carbon black. But which one?

Before getting to the roots of that question, the effect of the initial iron loading on the activity is looked at. Three series of catalysts were synthesized: CB/0 (no iron acetate added), 0.2, and 0.4% Fe/950 °C. In each series, the heat-treatment duration was varied. It is to be noted that carbon blacks contain metal impurities, including iron, with concentrations usually about 2−8 $\times 10^{-3}$ wt %. Catalysts of the series CB/0% Fe never exceed an activity of 0.1 mA mg^{-1} while the series CB/0.2 and 0.4% Fe achieve 2.4 and 2.8 mA mg^{-1}, respectively (Figure 2A). Consequently, 95−97% of the activity of the best catalysts stems from iron added onto the carbon black, not from iron native of the carbon black. The curves of activity with 0.4 and 0.2% Fe are almost superimposed, indicating that 0.2% Fe is close to the maximum initial loading convertible into active sites. This is in line with previous findings.[12−13,20] Surprisingly, even only 0.2% Fe on the carbon black lowers its reaction rate with ammonia (Figure 2B). This indicates that some ammonia must be decomposed by iron. At $T > 900$ °C there is a high thermodynamic driving force for NH_3 decomposition into N_2 and H_2 which can be catalyzed by metallic iron.[21] If some NH_3 is decomposed by Fe, then the gas in the surroundings of the catalyst powder, during catalyst preparation, will not be pure NH_3 but a mixture of NH_3, H_2, and N_2. Since H_2 reacts more slowly with carbon than ammonia,[14] it explains the suppressed weight loss with increased initial iron loading seen in Figure 2B.
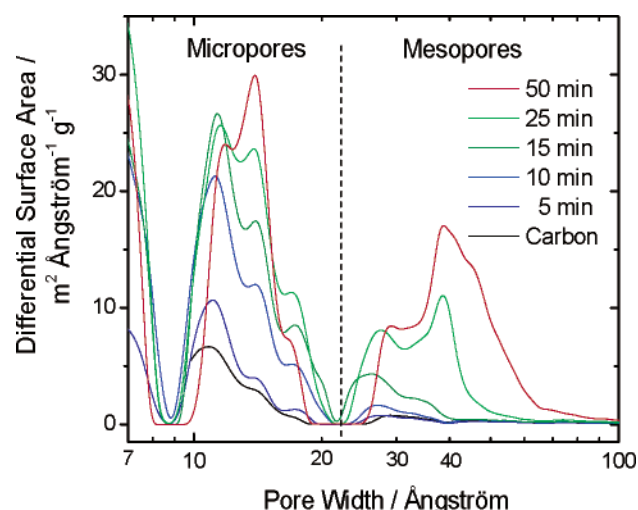
In the following, a structural characteristic of the catalysts is sought after that could account for the 2-decade disparity in activity seen in Figures 1 and 2.

The first parameter that needed examination was the N content of the catalysts since many catalysts synthesized at our laboratory had shown increased activity with higher N content.[14,22,23] Like the activity, the N content of all catalysts of Figure 1 is determined by the weight loss (Figure 3). At first glance, the activity roughly correlates with the N content and this seems like an attractive explanation. However, this explanation is ruled out by the chasm between the magnitude of change in N content (2-fold: 2 to 4 at. %) and in activity (factor 300:
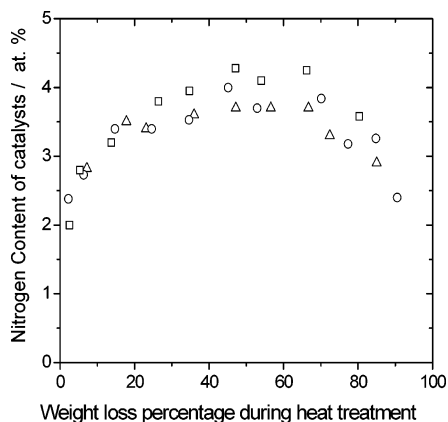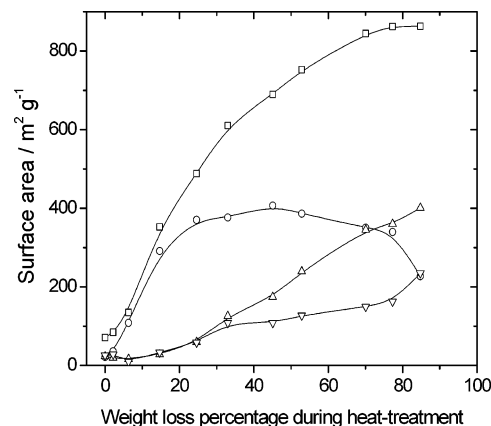
Figure 3. Effect of heat-treatment time and temperature on the N content of the catalysts. Nitrogen content of all catalysts of Figure 1A,B vs weight loss percentage of carbon during heat treatment. Time is a covert parameter. Heat treatment in pure NH_3 at 900 °C (□), 950 °C (○), and 1000 °C (△). All with 0.2 wt % Fe initial loading.

Figure 5. Surface area of three types of pores vs the time of heat treatment. Total surface area (BET, □), surface area imparted by micropores (width <22 Å, ○), mesopores (width 22−100 Å, △) and macropores (width >100 Å, ▽) vs the weight loss of carbon. Time of heat treatment is a covert parameter. All catalysts with 0.2 wt % Fe initial loading. Heat treatment in pure NH_3 at 950 °C.
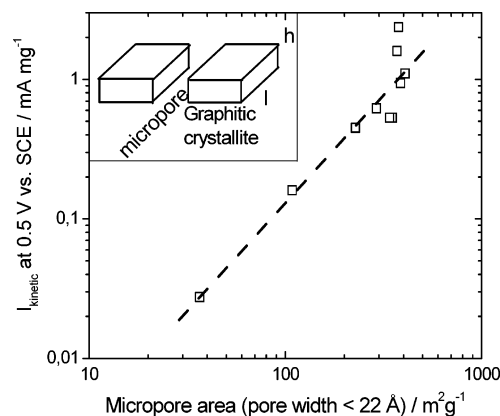

Figure 4. Effect of heat-treatment time on the pore-size distribution. Pore-size distribution of the as-received carbon black and of the catalysts after various times of heat treatment (time legend in figure) at 950 °C in pure ammonia. All catalysts with 0.2 wt % Fe initial loading (except for the carbon: no added iron acetate).

Figure 6. Activity for the O_2 reduction vs microporous area of catalysts. Kinetic current at 0.5 V vs SCE vs the surface area imparted by micropores (pore width <22 Å). Catalysts made with various times of heat treatment at 950 °C in pure NH_3. All catalysts with 0.2 wt % Fe initial loading. Insert: representation of a slit micropore.

0.01 to 3 mA mg^{-1}). One could retort that the nitrogen−carbon bonds may change, but this hypothesis is dismissed since all N_{1s} spectra look alike and their relative amount of pyridinic nitrogen is constant (about 35%, peak position 398.1 ± 0.1 eV). A detailed account of the reason a correlation between N content and activity was previously observed is given in the Supporting Information. In conclusion, the nitrogen content is not the factor limiting the site density in the present experimental conditions. After all, this is not surprising since 2−4 at. % nitrogen is 50− 100 times the iron concentration (0.2 wt % Fe translates into 0.04 at. % Fe) whereas an active site is believed to be of the type FeN_2C_x or FeN_4C_x.

Next, we investigated the pore structure of the catalysts. Porosimetry measurements were made on the catalysts CB/0.2% Fe/950 °C, heat-treated for various times in NH_3 (activity reported in Figure 1A, open circles). There are several striking features in the pore-size distributions (Figure 4). First, there are no pores of width 8.5−9 Å and of width 21.5−22.5 Å, regardless of the heat-treatment duration. Second, the surface area created by pores of width 7−22 Å increases tremendously from the pristine carbon black to catalysts made with increasing times of heat treatment, up to a time of 20−25 min. Beyond

that time, the area in this domain decreases (except in the 12.5− 15 Å region). In contrast with this, the area created by pores of width 22−100 Å increases constantly with increasing time of heat treatment. The results are presented in a denser form (Figure 5), splitting the total surface area into a microporous (created by pores of width <22 Å), a mesoporous (pore width 22−100 Å), and a macroporous surface area (pore width >100 Å). While the BET, the mesoporous, and macroporous areas steadily increase with increasing weight loss, the microporous area reaches a maximum at a weight loss of about 40% and decreases slowly afterward. The behavior of the micropore area with weight loss as well as the magnitude of its change resemble that seen for the catalytic activity and are a strong indication that the microporous surface area is the factor limiting the catalytic activity (site density) in the present experimental conditions. This is further evidenced by the plot of the catalytic activity as a function of the microporous surface area for the same series of catalysts (Figure 6). The figure is drawn in a log−log plane. Thus, a straight line corresponds to a power law of type $I_{kinetic}$@0.5 V vs SCE $= A \cdot (S_{micropore})^B$. With $I_{kinetic}$ in mA mg^{-1} and $S_{micropore}$ in $m^2 g^{-1}$, the fitting (line in Figure 6) yields $B = 1.55$. That B is greater than 1 should mean an activity increasing faster than linearly with the micropore area. Probably not all micropores of width <22 Å are capable of hosting the

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active sites, but only those satisfying a more stringent, yet unknown, condition on their pore-width value.

Thus, time *and* NH$_3$ are required to create micropores at high temperature in the carbon black, but once N-rich micropores exist, what is needed to form active sites? It follows from the results presented thus far that the synthesis is amenable to a two-step heat treatment where the formation of micropores is achieved in the first heat treatment and the formation of active sites in the second. The carbon black was treated for 12 min at 950 °C in pure ammonia, yielding $W = 24 \pm 1\%$ (point A in Figure 1C). That heat-treated carbon contains 3.5 at. % N. Then 0.27 wt % Fe was adsorbed. It is notable that, without a second heat treatment, adding iron acetate on the treated carbon does not modify its activity. The second heat treatment was performed at the lower temperature of 900 °C in either argon or ammonia (Figure 1C, catalysts A1−2 or A3−5, respectively). With argon (and despite retained N content of 3.5 at. %) the activity reached is 1 order of magnitude smaller than that obtained at $W \sim 25\%$ with a single heat treatment in ammonia (Figure 1C: A1−2 crosses vs open-square curve). In contrast, with NH$_3$ atmosphere during the second heat treatment, one obtains almost the same activity as that given by a single heat-treatment synthesis (Figure 1C: filled squares A4−5 and open-square curve at $W \sim 25\%$). This is also true at, e.g., $W \sim 70\%$ (Figure 1C, filled squares B1−2). The need for ammonia during the second heat treatment suggests that either mobile nitrogen atoms, or hydrogen atoms, are required if an iron is to construct an active site. Moreover, the results from Figure 1C tell us that only 5−12 min at 900 °C in ammonia was required to form a maximum number of active sites on the heat-treated carbon black (filled squares A4−5 in Figure 1C; site formation exclusively), whereas it took 40−50 min at 900 °C in ammonia to form a similar number of active sites when starting with the pristine carbon black (open squares in Figure 1A, micropore and site formation). Thus, at a given temperature, site formation is faster than micropore formation.

Discussion

Why Are Micropores Crucial for Catalytic Activity? The reported results strongly support the case that micropores are required to obtain good catalysts with the present synthesis method. This requirement suggests that the distance between two pore walls must have an exact value for a site to be formed. This in turn suggests that the catalytic site is a molecular assembly bridging two pore walls. The form and dimensions of these walls can be deduced from the following: micropores are believed to be formed by the anisotropic NH$_3$ etching of the carbon black; disordered carbon, found between graphitic domains, reacts faster than graphitic crystallites.[19] The latter are, in furnace carbon blacks, about 25−30 Å long and 12−14 Å thick (3−4 graphene layers).[24] Thus, a slit micropore (insert in Figure 6) should have walls about 20 Å long and 10 Å wide. Assuming that one micropore hosts one active site (coordinating one iron ion), the maximum iron loading, m_{Fe}, that can be coordinated for a given area of proper micropores, S_m, is $m_{Fe} = (S_m/2hl)(M_{Fe}/N_a)$, where h and l are the width and length of the micropore walls, M_{Fe} is the molecular mass of iron, and N_a is Avogadro's number. With $S_m = 400$ m^2 g^{-1} it yields $m_{Fe} = 0.93$ wt % ($h = 10^{-9}$ m, $l = 2 \times 10^{-9}$ m, $M_{Fe} = 55.8$ g mol^{-1}, $N_a = 6.02 \times 10^{23}$). This value is close to the upper utilizable limit of 0.2−0.5 wt % of metal-on-carbon faced experimentally.[12,13,20]

Review of Previous Works with Micropores in Mind. Though restricted to results obtained on a single carbon black and iron acetate in the present study, the micropore explanation

seems to clarify results previously obtained with other carbons or other metal precursors. Reanalyzing a previous work[14] and extending it to other carbon blacks, we showed that the activity unmistakably increases with increased weight loss (in the range of 0−40 wt %) during heat treatment in ammonia.[19,25] In those studies, the change in weight loss was inherent to the carbon sample because the time of heat treatment was fixed. The reader can check Tables 3 and 5 in ref 14 and conclude that the activity increases with increased micropore area, except for two catalysts prepared with Norit and one prepared with Black Pearls. In another work, the activity of catalysts prepared with various carbon blacks and with two Fe precursors (acetate or porphyrin) displays a maximum activity at a BET area of about 700 m^2 g^{-1}.[23] This is also the BET value found in this study at a weight loss W of 35%, position at which the activity and micropore surface area are maximized (Figures 1 and 5). We are presently investigating carbon blacks of different grades heat-treated for various times in NH$_3$. They all display an optimum of activity similar to the one observed in Figure 1B.

Conclusions

In summary, the state-of-the-art activity (site density) of Fe-based electrocatalysts seems limited, in the present experimental conditions, by the cumulative surface area of micropores with width up to 22 Å. The density of active sites formed at high temperature reaches its maximum when (i) Fe is present, (ii) the surface area of micropores of width <22 Å in the carbon black is maximized, and (iii) NH$_3$ is present. Requirement (ii) is fulfilled in this study through anisotropic reaction of NH$_3$ with the initially non-microporous carbon black. The etching reaction incorporates nitrogen atoms in the structure of the carbon support. The catalysts can be synthesized either in a single heat treatment or by two heat treatments, depending on whether the micropore formation is concomitant with site formation (single heat treatment: carbon, Fe, and NH$_3$) or if these two processes are separated (heat treatment 1: carbon and NH$_3$; heat treatment 2: heat-treated carbon, Fe, and NH$_3$). In heat treatment 2, NH$_3$ is again required in order to react with iron ions and form active sites. Nitrogen atoms incorporated in the carbon structure during heat treatment 1 do not suffice to complete sites.

Supporting Information Available: Description of oven stabilization and calibration; equal validity of both techniques (rotating or not-rotating the disk electrode) for catalytic activity measurement; full E−log I plots whereof the kinetic current at 0.5 V vs RHE is derived, discussion on macroscopic activity, single-site activity, and site density; why was there a correlation between activity and N content in previous studies? This material is available free of charge via the Internet at http://pubs.acs.org.

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