

1 Experimental study of characteristics of bimetallic Pt-Fe nano-particle fuel 2 cell electrocatalyst

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7 Abstract

8 The characteristics of 1.5 wt% Platinum (Pt) loading on Fe incorporated Y zeolite (Pt-Fe/Y zeolite) nano-
9 electrocatalysts have been experimentally studied by the extended X-ray adsorption fine structure (EXAFS)
10 and cyclic voltammetry (CV) techniques using Nafion[®] bound electrode to determine Pt electrocatalytic
11 performance in direct methanol fuel cell. The Pt particle size was found to be small in electrochemical
12 environment (0.7 nm with 55 atoms). Study implies that the Pt electrocatalytic performance can be affected
13 by the Pt cluster electron deficiency, due to the change of Pt particle size associated with the lattice strain
14 energy. The CV measurement in the hydride region indicated higher Pt dispersion for Pt-Fe/Y zeolite
15 electrocatalyst chemically reduced in H₂ at 400°C (15PtFeancr4), compared to that of Pt/Y zeolite reduced at
16 400°C (15Ptancr4) and Pt-Fe/Y zeolite electrocatalysts reduced at 300°C (15PtFeancr3), respectively. This
17 provided further implication that the chemical reduction temperature would be important for achieving a
18 higher Pt dispersion. The present study has revealed two possible electron transfer pathways that might
19 contribute to the Pt electronic conduction: (1) the surface mobility of adsorbed species; (2) the hydrogen
20 atoms/H⁺ ion spillover through the zeolite framework and on the electrode surface, despite the DC insulator
21 nature of zeolite.

22
23 **Keywords:** Bimetallic nano-particle fuel cell, Pt-Fe/Y zeolite, Electrocatalytic performance, Bonding
24 distance, Extended X-ray adsorption fine structure, Cyclic voltammetry (CV).

25 1. Introduction

26 Fuel cell has been widely used as an alternative clean energy converting device for many applications, such as
27 mobile phone, portable laptop and hybrid car, because of its unique properties such as zero/low emission,
28 high energy efficiency, and potentially high power density [1, 2]. However, the high cost and short lifespan of
29 Pt as electrocatalyst materials represent two major technical challenges that slow down the progress of fuel
30 cell commercialization, especially for domestic applications. So far, the most promising fuel cell electrocatalyst
31 is the high-loading carbon supported Pt [3, 4]. In recently studies, zeolite has been used as Pt supported
32 substrate in cathode proton exchange membrane (PEM) fuel cell [5, 6] and also as electrode for methanol
33 oxidation, in which the Pt particle size has played an important role in improving the fuel cell electrochemical
34 oxidation and reduction activity [7]. While it was reported that the Pt catalytic activity could be enhanced with
35 increase in Pt surface area [8], there was little understanding on the contribution of protons or auxiliary metal
36 ions (e.g. Fe) as chemical anchors to improve Pt dispersion thus to reduce the Pt particle size and to enhance
37 the electron/charger transfer between Pt and Pt on the metal supporting substrate (i.e. zeolite framework)
38 under electrochemical control. These issues will be addressed in this study.

39 Based on zeolite structure characteristics, metal particles can be stabilised on zeolite Brønsted active sites
40 through the interaction with protons or auxiliary metal ions, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the interconnected
41 microchannels, and also cages of microporous material, such as NaY zeolite [9]. In a Pt-Fe bimetallic system,
42 strong interactions between Fe ions and zeolite substrates can further stabilize the Pt particles at zeolite
43 surface by anchoring Pt on zeolite active sites to prevent the sintering of Pt metal particles at high
44 temperature in order to achieve a highly dispersed Pt state [10]. Moreover, the catalytic performance of a Pt-
45 Fe zeolite catalyst system can be largely enhanced compared to that of a Pt zeolite catalyst. It was revealed by
46 Hwang and Chung [11] that the specific activity in a Pt-Fe bimetallic system might be partially altered due to
47 the change of Pt-Fe local density resulting in the narrowing of the metal d-band in molecular orbit, rather than
48 being directly influenced by the Pt-Fe particle size. The locations of Pt and Fe particles are also crucially
49 dependent on the stoichiometry of the titration method (O_2 , H_2) [11].

50 It was known that in a gas atmosphere, the metal alloy behaviour could be greatly affected by O_2 and H_2 due to
51 the presence of high reactivity being driven towards the zeolite surface. The Hydrogen chemisorption presents

52 a major chemical process to control Pt particle size during the Pt calcination and reduction process [12]. As a
53 result, Pt particles can remain in the zeolite supercages at a temperature of 300°C with measured particle sizes
54 between 6Å and 13Å. However, Rolison et al. [13] has observed larger Pt particle sizes of greater than 2nm.
55 Their study indicated that the Pt could migrate into sodalite cages and hexagonal prisms at H₂ reduction
56 temperatures of 600+°C, and remain in a stable status inside the sodalite cages, particularly in the hexagonal
57 prisms with high charge density. A previous study of using the extended X-ray adsorption fine structure
58 (EXAFS) [10] has predicted the contraction of Pt–Pt bonding distance on zeolite with the following
59 observations: (1) increase in Pt-Pt bonding energy with electron deficiency, leading to a change in local density
60 between the zeolite substrate and the Pt-Fe particle; (2) decrease in the overlapping of metal d-band among
61 the Pt and Fe elements. A further study [14] also revealed that additional Pt atom thermal disorder and Pt-Pt
62 bonding energy increase might lead to an increase in Pt particle size, and consequently a reduction in Pt
63 electro-catalytic performance.

64 The study of Fe²⁺/Fe³⁺ ion oxidation/reduction on zeolite indicates that Fe²⁺ ion favourably remained in zeolite
65 supercages [15, 16]. An enrichment of Fe²⁺ at the zeolite surface was mainly attributed by the particle size
66 related high lattice strain energy (see, e.g. [10]). In contrary, the Fe³⁺ ion with high charge density would more
67 likely migrate to small channels, leading to the blockage of zeolite sodalite cages and hexagonal prisms. The Pt
68 entrapped in zeolite cages can form particle size ranging from a single atom [13] to a cluster of 10 to 25 atoms
69 of average 1 - 2 nm in size [17].

70 Despite these findings, the electronically conducting mechanism of Pt or Pt bimetallic particle on zeolite in an
71 electrochemical environment is still not well understood. The most common hypothesis of electrocatalytic
72 reaction in Pt zeolite system is the H⁺ ion 'spillover' pathway, which might involve electrocatalytic reaction on a
73 Nafion[®] based Pt zeolite electrode due to the nature of zeolite ionic conduction. Furthermore, the hydrogen
74 'spillover' in a Pt zeolite electrode system may interact with not only the Brønsted site but also the Lewis site
75 of the zeolite, in which protons act as a catalytic active site for catalysed acidic reaction [18]. The surface
76 diffusion and the 'spillover' of H-ad atoms associated with oxygen-containing surface species provide another
77 pathway to promote the electrochemical reaction in addition to the pathway of surface conductance. The
78 electrocatalytic process on Pt zeolite carbon mixed porous electrodes implicated by the cyclic voltammetry
79 (CV) measurement has supported the assumption made on the charge associated Pt zeolite surface

80 conductance, which involves the acidic oxide species on the carbon surface [19]. Meanwhile, the
81 electrochemical potential regime has significant impact on the surface conductivity pathway and the
82 hydrogen/oxygen 'spillover' pathway in an electrode system, in which the electrode surface condition may be
83 changed. In a Pt/Co electrode system, hydrogen (H^+) ions and oxygen-containing surface species can cause the
84 'spillover' at the Pt surface. Nevertheless, the Pt-Fe/Y zeolite catalyst may adopt a similar electrocatalytic
85 pathway of H^+ ion 'spillover'. It was found that a 'spillover' phenomenon occurred when the electrochemical
86 reaction took place during the surface diffusion process of absorbed species [18], leading to the migration of
87 hydrogen ions (H^+). Furthermore, the surface conductivity may possibly involve in the electrochemical process
88 since the zeolite is an ionic conductor. In this regard, the hydrogen 'spillover' pathway in a Pt-Fe/Y zeolite
89 electrode system has not been fully understood and thus more researches are required in the field.

90 In this study, the Fe^{2+} ion is chosen as an auxiliary metal to study the Pt migration in a Nafion[®] bound zeolite
91 electrode system for highly dispersed Pt distributions. The effect of auxiliary metal functions of Fe^{2+}/Fe^{3+} on Pt
92 particle size and Pt-Fe, Pt-Pt neighbouring distances in a Pt-Fe Zeolite system will be investigated using EXAFS
93 technique in a hydrogen/oxygen gas purged cell and in a electrochemical cell with H_2SO_4 electrolyte solution.
94 The CV measurement will also be performed to ascertain the Pt electrocatalytic activity associated with the
95 hydrogen adsorption/desorption peaks in the hydride region. Finally, experimental results will be analysed to
96 reveal the Pt zeolite electrochemical conducting mechanism in Pt/Y or Pt-Fe/Y zeolite carbon powder Nafion[®]
97 bound electrode system, and to authors' knowledge this has not been fully explored in published literatures.

98 **2. Experimental**

99 2.1 Preparation of Pt-Fe Y zeolite Electrocatalysts

100 The 1.5 wt% Pt loading Pt/Y zeolite and Pt-Fe/Y zeolite electrocatalysts were prepared in the Laboratory
101 environment, where the Fe^{2+} underwent ion exchange with zeolite ion in the acidic solution stirred by an
102 ultrasonic bath. The sample was then fully dried and calcined at 350 °C in a fluidised bed purged with gas air.
103 The resultant sample subsequently underwent ion exchange with the $Pt(NH_3)_4(NO_3)$ solution at neutral pH
104 until no Pt ions in the ion exchanged solution is detected by UV spectroscopy [20]. The final Pt-Fe zeolite
105 products were dried overnight in an oven after being washed by triple distilled water.

106 The synthesis of Pt or Pt-Fe alloy microstructures on Y zeolite followed the calcination and reduction
107 procedure developed by Gallezot and his co-workers [21]. This involves the removal of Pt and Fe coordinated
108 ligand, i.e. Pt/Y and Pt-Fe/Y zeolite electrocatalysts were purged with argon at a moderate temperature in a
109 fluidized bed reactor fitted with 10 μm pore glass frit. For 1.5 wt% Pt loading Pt-Fe zeolite sample, the
110 calcination process was carried out in O_2 at 350 $^\circ\text{C}$, followed by H_2 reduction at 300 $^\circ\text{C}$ (denoted as
111 15PtFeancr3) and 400 $^\circ\text{C}$ (denoted as 15PtFeancr4), respectively. The 1.5 wt% Pt loading on Y zeolite
112 electrocatalyst was calcined at 350 $^\circ\text{C}$ in O_2 and later reduced at 400 $^\circ\text{C}$ in H_2 (denoted as 15Ptancr4).

113

114 2.2 Electrochemical cell and cyclic voltammetry

115 The electrode was made of Pt-Fe/Y zeolite and (untreated) XC-72R carbon powder mixtures added with 15
116 wt% Nafion[®] (i.e. 5 wt% solution in Aliphatic Alcohols and H_2O from Aldrich) conductive electrolytic polymer as
117 a binder. The resultant 'hot' paste was pressed on carbon paper (E-TEK TGHP-90) for solidification. A disc of
118 2.5cm diameter of electrode was then cut for cyclic voltammetry measurement using a glass-jacketed
119 electrochemical cell, consisting of working Pt electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ Mercury/Mercurous Sulfate (MMS)
120 reference electrodes incorporated with a Pt gauze counter electrode. A 1.3 cm diameter working electrode
121 was later adopted for the EXAFS measurement.

122 The in-situ EXAFS measurement was carried out in an electrochemical cell formed by two acrylic discs with two
123 Kapton windows cut in the middle, in which a working electrode was placed by one acrylic disc accomplished
124 by a gold wire current collector placing underneath the Pt-Fe/Y zeolite working electrode to reinforce the
125 contact in the cell system via Pt gauze. The Pt-Fe/Y zeolite working electrode was kept within several layers of
126 filter papers soaked in 1 mol dm^{-3} H_2SO_4 solution to prevent the electrode drying out. The $\text{Hg}/\text{Hg}_2\text{SO}_4$ MMS
127 reference electrode was then connected to the electrochemical cell via a salt bridge, re-assembled to produce
128 a sufficiently large absorption edge for EXAFS measurement.

129 The electrolyte was 2.5 mol dm^{-3} sulphuric acid (H_2SO_4) solution used for Laboratory cyclic voltammetry
130 measurement and 1 mol dm^{-3} sulphuric acid (H_2SO_4) for the in-situ EXAFS measurement using a computer-
131 controlled potentiostat (Auto-Lab PGSTAT20), respectively. The working electrode was controlled by a

132 potential ramp from waveform generator at a constant scan rate (dE/dt) of 1 mV/s [22]. The
 133 oxidation/reduction of the electro-active species of interest on Pt-Fe/Y zeolite electrode was detected by a
 134 current change in the potential region of -0.65 V to 0.5 V, in which no solvent and electrolyte decomposition
 135 occurred [23].

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137 2.3 Extended X-ray adsorption fine structure (EXAFS)

138 The Extended X-ray Absorption Fine Structure (EXAFS) measurements were performed using the Synchrotron
 139 Radiation Source (SRS) at Daresbury Laboratory, UK. The wiggler beam line was operated at 2 GeV and 100
 140 mA, and the high-order harmonics that may affect the amplitude of EXAFS were removed using a double-
 141 crystal Si220 monochromator. The 50% detuning of a harmonic beam was used to locate the Pt L_{III} absorption
 142 edge, e.g. using gas - ion chambers filled with Ar, Xe or Kr and He. A Pt foil was used as a reference sample for
 143 EXAFS data collection.

144 Data analysis was carried out using software EXCALIB, EXBROOK and EXCURV 98. The inter-atomic distance,
 145 atom number and type of backscattering neighbours were determined, based on following equations as [24]

$$146 \quad A_j(k) = (N_j / 2k R_j) S_0^2 F_j(k) e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)}, \quad (1)$$

$$147 \quad \chi_k = \sum_{j=1}^{shell} (N_j / 2k R_j) S_0^2 F_j(k) e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} \sin[2kR_j + 2\phi_{absorbance}(k) + \phi_{backscattered}(k)], \quad (2)$$

$$148 \quad FT(r) = 1/\sqrt{2\pi} \int_{min}^{k_{max}} k^n \chi(k) \exp(-2ikr) dk, \quad (3)$$

149 where N_j is the number of neighbouring atoms of type j with backscattering amplitude F_j(k), which is
 150 dependent on the neighbouring atom number. S₀ is an amplitude reduction term that takes into account the
 151 body effect such as shake-up and shake-off process due to multi-electron excitation and energy loss [24]. The
 152 term $e^{-2k^2\sigma_j^2}$ is the Debye Waller factor which represents a measurement of static and thermal disorder in
 153 the sample and is temperature dependent. λ_j(k) is the mean free path length of the photo electron. φ is the

154 outgoing and backscattering electron wave function of the core atomic potentials of the emitting atom and
155 backscattered atom. X_k is the function of EXAFS. k is measured in \AA^{-1} . A_j is the wave amplitude.

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157 **3. Results and Discussion**

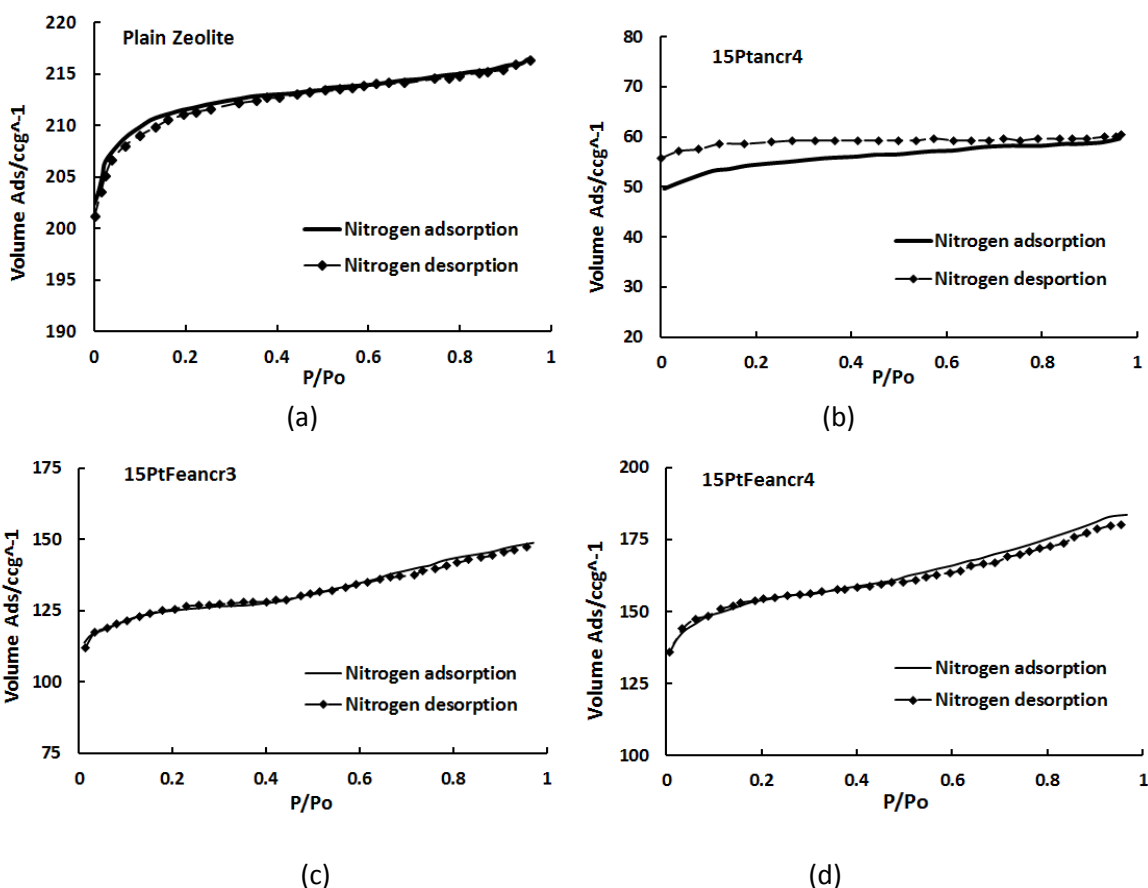
158 3.1 Zeolite BET surface areas measurement

159 The Brunauer-Emmett-Teller (BET) surface area measurement and X-ray diffraction (XRD) characterization
160 were employed primarily to investigate the change of zeolite crystalline structure. Figure 1 depicts the zeolite
161 BET surface area measurement for the three electrocatalysts 15Ptancr4, 15PtFeancr3 and 15PtFeancr4,
162 respectively. The measurement of a plain zeolite sample was used for reference, in which the surface area of
163 $632 \text{ m}^2\text{g}^{-1}$ was determined. For Fe incorporated catalysts with 1.5wt% Pt loading on zeolite either reduced at
164 $300 \text{ }^\circ\text{C}$ (i.e. 15PtFeancr3) or at $400 \text{ }^\circ\text{C}$ (i.e. 15PtFeancr4), the surface areas of two zeolite samples were very
165 close and measured at $371 \text{ m}^2\text{g}^{-1}$ and $346 \text{ m}^2\text{g}^{-1}$, respectively. This is almost twice as large as the value (168
166 m^2g^{-1}) given by the catalyst with 1.5 wt% Pt loading on zeolite reduced at $400 \text{ }^\circ\text{C}$ (i.e. 15Ptancr4). While
167 compared to the plain zeolite surface area, the discrepancy is about $261 - 286 \text{ m}^2\text{g}^{-1}$. The BET measurement
168 indicates that the surface area of zeolite crystallized structure of the Fe incorporated Pt zeolite electrocatalysts
169 (both 15PtFeancr3 and 15PtFeancr4) is preserved relatively well, in comparison to that of Pt zeolite
170 electrocatalyst (i.e. 15Ptancr4). The reduction of zeolite surface area indicates that the collapse of crystallized
171 zeolite structure is predominant during the calcination and reduction process, leading to the blockage of
172 zeolite opening pores in small channels. This has been further confirmed by X-ray diffraction (XRD)
173 measurements, as presented in figure 2.

174 The XRD data were collected by using an impinging or a reflected X-ray beam at an incident angle of $2\text{-}\theta$
175 (θ) in a range of $5^\circ - 44^\circ$ at room temperature. The XRD measurements were primarily used to qualitatively
176 examine the zeolite crystalline structure changes due to thermal treatment with metal disposition. Comparing
177 to that of a standard plain zeolite [25], the XRD pattern has shown a significant reduction of the diffraction
178 peak intensity by a maximum factor of 10 for sample 15Ptancr4 and a maximum factor of 100 for Fe
179 incorporated samples 15PtFeancr3 and 15PtFeancr4, together with a slight 'shift' of peak positions. The XRD

180 pattern baseline and noise level of spectra for Fe incorporated Pt zeolite catalysts is found to be very high,
 181 which indicates a structure disorder resulting from the ‘collapse’ of the zeolite crystallite structure. The XRD
 182 spectra exhibit similar patterns for all types of Pt and Pt-Fe/Y zeolite electrocatalysts studied. As the Pt
 183 deposition quantity is relatively small, the decrease of zeolite surface area may imply the blockage of the
 184 smaller pores owing to the collapse of zeolite structures during the calcination and reduction process,
 185 particularly for Fe incorporated Pt catalysts (i.e. 15PtFeancr3 and 15PtFeancr4). Conclusively, the XRD spectra
 186 have confirmed the BET surface area measurements for zeolite structural change [25]. Table 1 displays a
 187 comparison of zeolite surface area of the corresponding electrocatalysts. It can be seen that the zeolite surface
 188 area for 1.5wt% Pt/Y zeolite electrocatalyst (i.e. 15Ptancr4) is the smallest, implying that the ‘collapse’ of
 189 zeolite crystalline structures might be severe, compared to Fe incorporated samples 15PtFeancr3 and
 190 15PtFeancr4.

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198 Figure 1. Volumetric uptake of Nitrogen at 77K with absorption in solid lines, and desorption in solid line with
 199 symbols. (a) plain zeolite; (b) 1.5 wt% Pt loading on zeolite calcined at 350 °C and reduced at 400 °C
 200 (15Ptancr4); (c) 1.5 wt% Pt loading on Fe incorporated zeolite calcined at 350 °C and reduced at 300 °C
 201 (15PtFeancr3); (d) 1.5 wt% Pt loading on Fe incorporated zeolite calcined at 350 °C and reduced at 400 °C
 202 (15PtFeancr4).

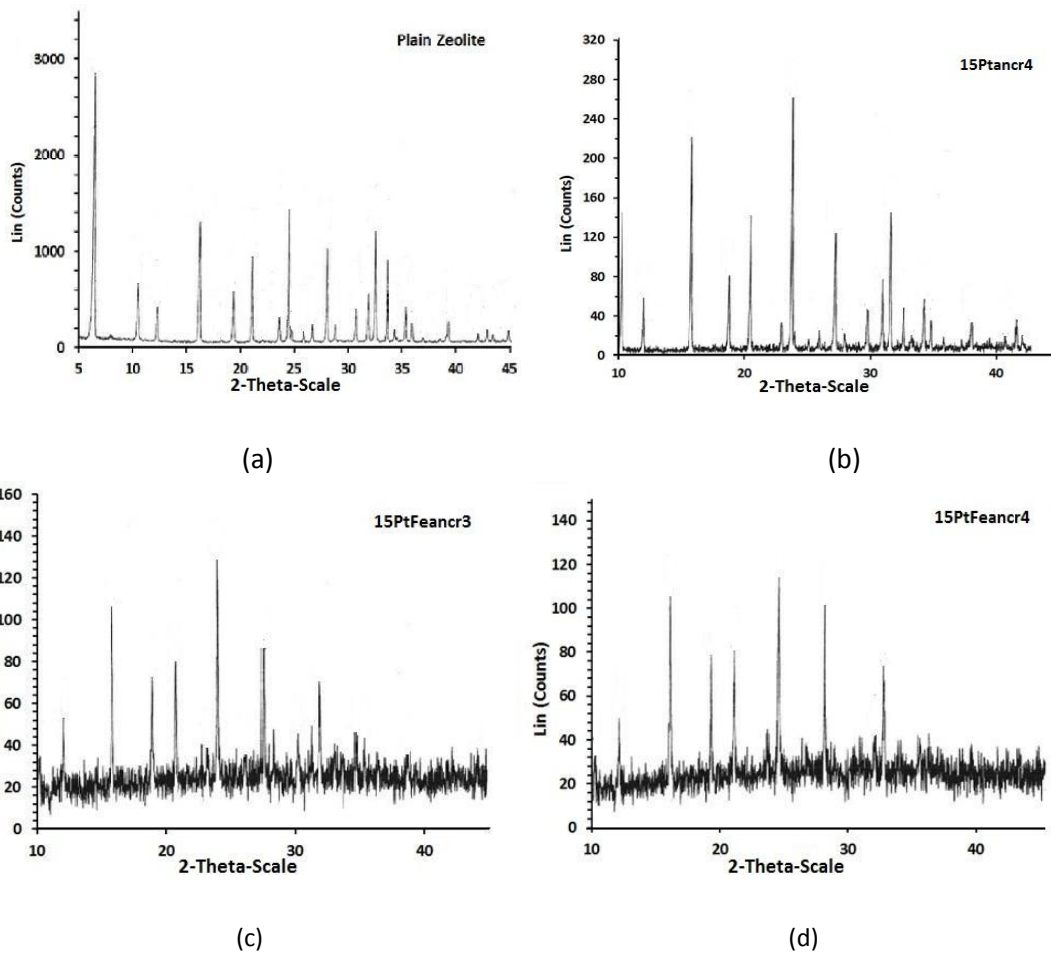
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204 Table 1. The BET surface area measurements for plain zeolite, Pt zeolite and Fe incorporated Pt zeolite
205 electrocatalysts. The measurement error is between 0.1% and 10%.

Acronym Name	Surface Area m ² /g
Plain Zeolite Catalyst	623.2 ± 0.1%
15Ptancr4 Catalyst	168 ± 10%
15PtFeancr3 Catalyst	371 ± 5.0%
15PtFeancr4 Catalyst	346 ± 3.0%

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215 Figure 2. The X-Ray Diffraction (XRD) patterns, (1) plain zeolite; (2) 15Ptancr4; (3) 15PtFeancr3; (4)
216 15PtFeancr4. Theta (θ) is the Bragg angle of incidence or reflection of the X-ray beam, and Lin (counts) is the
217 unit of X-ray intensity.

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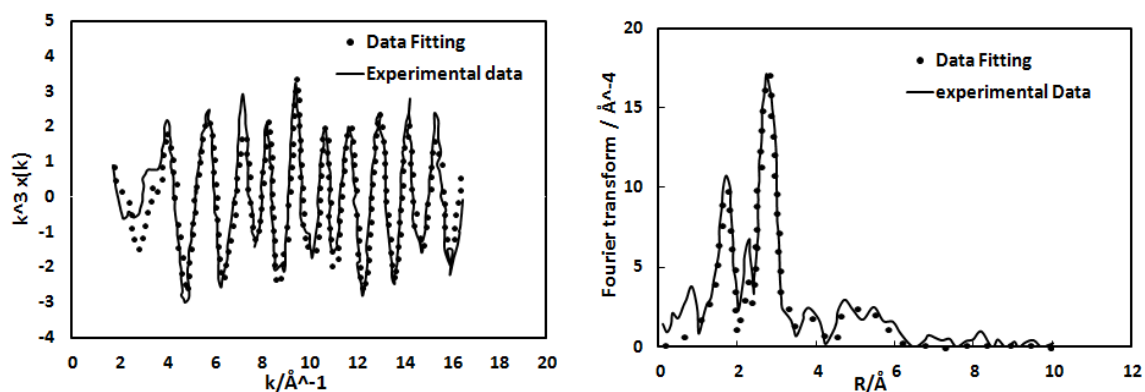
219 3.2 The ex-situ EXAFS measurement for 1.5 wt% Pt electrocatalyst on zeolite (15Ptancr4) without Fe

220 3.2.1 1.5 wt% Pt loading Pt/Y zeolite electrocatalyst

221 The pellet was employed for the ex-situ EXAFS measurement using 1.5 wt% Pt Y zeolite and boron nitride
222 powder mixture. It was placed between two pieces of plastic film in O₂ or H₂ purged gas cell at room
223 temperature. The EXAFS spectrum was taken at the Pt L_{III} edge and was then analysed using a computer code
224 EXCURV 98 developed at Daresbury Laboratory, UK.

225 Figure 3 depicts the k³ weighted EXAFS (Chi) data and its Fourier transforms (FT) presented in R-space. The
226 dotted symbols represent fitted results of the raw data. The amplitude of Chi data of sample 15ancr4 collected
227 in O₂ tends to exhibit insignificant oscillation. A maximum peak in R-space was found to be 2.76Å in the Fourier
228 transform (FT) spectrum, and a higher neighbouring shell was fitted at a peak value between 4Å and 6Å. Also
229 the Pt-O bonding distance in R-space is determined to be 2.02Å in the first Pt-O shell and the correspondent
230 oxygen number is approximately 1.23. The Pt-Pt distance in the second Pt shell is predicted to be about 2.76Å.
231 This closely resembles the metal Pt-Pt bonding distance, indicating a crystallographic network of Pt particles,
232 similar to that of Pt metal foil, which was used as background reference sample during data collection.

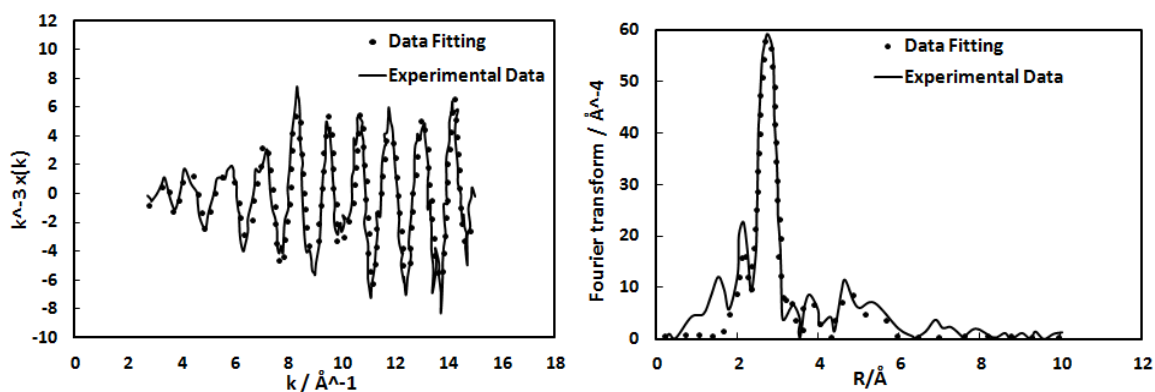
233 A progressive increase in the high *k*-value of the raw EXAFS spectrum amplitude and oscillation has been
234 determined by samples with 1.5 wt% Pt loading on Y zeolite (i.e. 15Ptancr4) in hydrogen purged gas cell (see
235 Fig. 3b). This suggests that Pt nano-particle has a longer neighbouring distance and a high *z*-value (i.e. atom
236 number) in neighbouring field within a short oscillation period. There is no neighbouring oxygen atom
237 predicted and the Pt-Pt distance at the Pt first shell was measured to be 2.75Å, indicating the metallic nature
238 of Pt nano-particles with the face centered cubic (FCC) structure of Pt metal. The Pt-Pt coordination number
239 (*N*) in the first shell was 6.33, a factor of 2 higher than a number of 3.13 predicted for the same sample treated
240 in gas cell purged with O₂ (i.e. shell 2 in Table 2a). In both cases, the Pt has fitted up to 4 shells. The overall Pt-
241 Pt coordination numbers fitted for data collected in H₂ cell (as seen in Table 2b) has 17 atoms, compared with
242 average number of 14.83 atoms fitted for data collected in O₂ cell. The results are in good agreement with that
243 given by Benfield [26]. In another similar study [27], the Pt-Pt coordination number was found to be 6.0 for a
244 Pt/Y sample calcined at 300 °C and reduced at 500 °C. This value also agrees well with that from the present
245 study for 1.5 wt% Pt on Y zeolite (i.e. 15Ptancr4).



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(a) In Oxygen gas



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(b) In Hydrogen gas

250 Figure 3. EXAFS data fitting for 1.5 wt% Pt loading Pt/Y zeolite catalysts (a) Data collected in gas cell purged by
 251 Oxygen, with phase correction; (b) Data collected in gas cell purged by Hydrogen, with phase correction. The
 252 experimental data are in solid lines and the fitted data are in dotted symbols, respectively. The EXAFS data was
 253 collected at Pt L_{III} edge. Sample 15Ptancr4 - calcined at 350 °C and reduced at 400 °C (i.e. 15Ptancr4).

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Table 2. Data fitting results for each Pt shell at Pt L_{III} edge

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(a) Data fitting results for sample 15Ptancr4 in O_2 gas at room temperature

15ancr4	Shell 1 - O	Shell 2 - Pt	Shell 3 - Pt	Shell 4 - Pt	Shell 5 - Pt
N	1.23	3.13	1.75	3.12	6.83
R (Å)	2.02	2.76	3.90	4.81	5.44

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(b) Data fitting results for sample 15Ptancr4 in H_2 gas at room temperature

15ancr4	Shell 1 - Pt	Shell 2 - Pt	Shell 3 - Pt	Shell 4 - Pt
N	6.33	0.88	3.34	6.40

R (Å)	2.75	3.91	4.78	5.42
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261 3.2.2 1.5 wt% Pt loading with Fe incorporated Pt-Fe zeolite electrocatalyst

262 3.2.2.1 Analysis of ex-situ EXAFS data collected at Pt L_{III} edge in O₂ at room temperature

263 The effect of auxiliary Fe²⁺ ions in assisting the Pt distribution on zeolite framework has been investigated using
 264 the EXAFS spectroscopy at Pt L_{III} edge and at Fe K-edge, in oxygen or hydrogen purged gas cell, respectively.

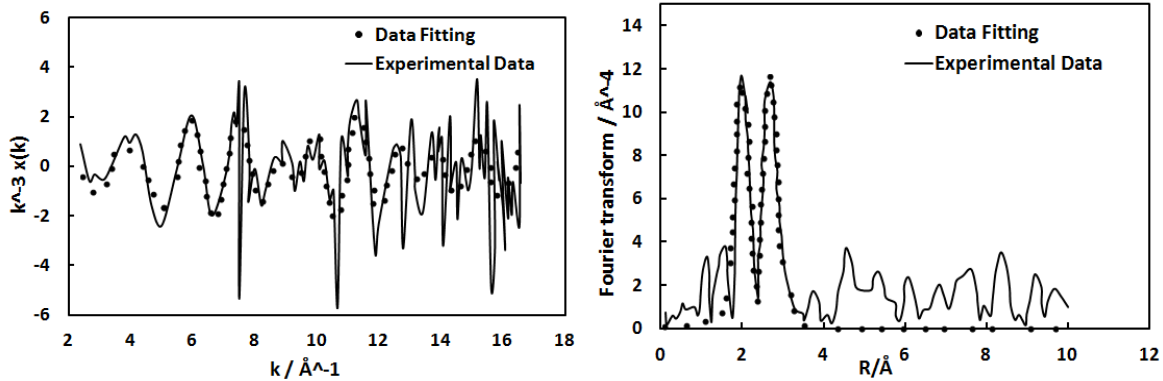
265 Figure 4 illustrates the EXAFS spectra and Fourier transforms, fitted in R-space by k^3 weighting for 1.5 wt% Pt
 266 loading catalyst on Fe incorporated Y zeolite purged in either O₂ or H₂. The data fitting results are shown in
 267 table 3.

268 A high noise level was found in the Chi data spectrum for 1.5 wt% Pt loading Pt-Fe metal alloy zeolite
 269 electrocatalyst calcined at 350 °C and reduced at 300 °C (i.e. 15PtFeancr3) and 400 °C (i.e. 15PtFeancr4),
 270 respectively, compared with that of 1.5 wt% Pt loading of Pt/Y zeolite electrocatalysts (i.e. 15Ptancr4). A high
 271 oxidation state was detected in sample 15PtFeancr3 with a correspondent O₂ coordination number of 0.92.
 272 The neighbouring coordination number of Pt and Fe are 1.26 and 0.54, respectively. The averaged Pt-O
 273 bonding distance is predicted about 1.99Å for sample 15Ptfeancr3 and 1.94Å for sample 15PtFeancr4,
 274 respectively, both having slightly shortened distances compared to a normal Pt-O bonding distance of 2.02Å in
 275 O₂ gas. It was found that the Pt fitting in the second shell had not shown similar agreement with those found
 276 in sample 15Ptancr4. A contraction of Pt-Pt bonding distance is predicted at 2.56Å and 2.57Å for sample
 277 15PtFeancr3 and for sample 15PtFeancr4, respectively, compared to 2.76Å for 1.5 wt% Pt loading on Y zeolite
 278 (i.e. 15Ptancr4). As observed and discussed by Mathew [28], the shortening of Pt bonding distance is possibly
 279 attributed to an additional third shell of Fe in the metal to form a Pt-Fe bimetallic particle, and this could result
 280 in a 'shift' of d-band energy to reduce the distance of the Pt-Pt bond in Fourier transform module. The Pt-Fe
 281 bonding distance is found 2.44Å for sample 15PtFeance4 and 2.59Å for sample 15PtFeancr3, respectively. The
 282 additional second shell fitting of Pt for sample 15PtFeancr4 has led to an improvement of a fitting value R_{exafs}
 283 to 47.73% with the Pt-Pt distance predicted at 3.99Å, and the Pt coordination number is measured to be 1.55
 284 in shell 1 and 1.00 in shell 2 correspondent to Fe and O₂ coordination numbers of 0.65 in shell 3 and 0.75 in

285 shell 1. The high neighbouring oxygen atom coordination number predicted for sample 15PtFeancr3 indicates
286 the incomplete reduction of Pt or Fe oxides at a moderate reduction temperature of 300 °C resulting in lower
287 quality of EXAFS data, as implied by a fitting value R_{exafs} of 59.71%.

288 For sample 15PtFeancr4, the multiple Pt shells of data fitting indicates that high percentage of Pt or Pt-Fe alloy
289 is located on the zeolite exterior surface at a relatively high reduction temperatures. The Pt particle reduced at
290 400 °C (i.e 15PtFeancr4) in H₂ gas may be more likely to remain in zeolite supercages or on zeolite external
291 surfaces in comparison to that reduced at a relatively low temperature of 300 °C (i.e. 15PtFeancr3). Other
292 researchers also obtained similar findings, i.e. a small fraction of metal particles was distributed on the exterior
293 of zeolite with little constrain from the internal architecture of zeolite structure [14, 29]. For Pt located at the
294 interior of the zeolite framework, an electron deficiency of Pt cluster has been observed previously [13] due to
295 the formation of a metal-proton adduct on zeolite acidic sites. The auxiliary metal ions, such as Fe²⁺ ion has
296 similar functionality as the proton in a zeolite system, where they assist in anchoring the Pt particle onto the
297 zeolite cage wall during the precursor thermal treatment. The Fe³⁺ ions are more favourable to remain in the
298 zeolite small cages, such as sodalite cages and hexagonal prism than the Fe²⁺ ion due to their high charge
299 density. The formation of a mixed oxidation phase by Fe²⁺ and Pt²⁺ ions can prevent the mobility of Pt-Fe
300 bimetallic alloy and thus leads to an increase in Pt distribution of zeolite. A further improvement of Pt stability
301 is also possible, and can be initiated by the interference of Pt and acidic oxidising species on zeolite surface
302 [10].

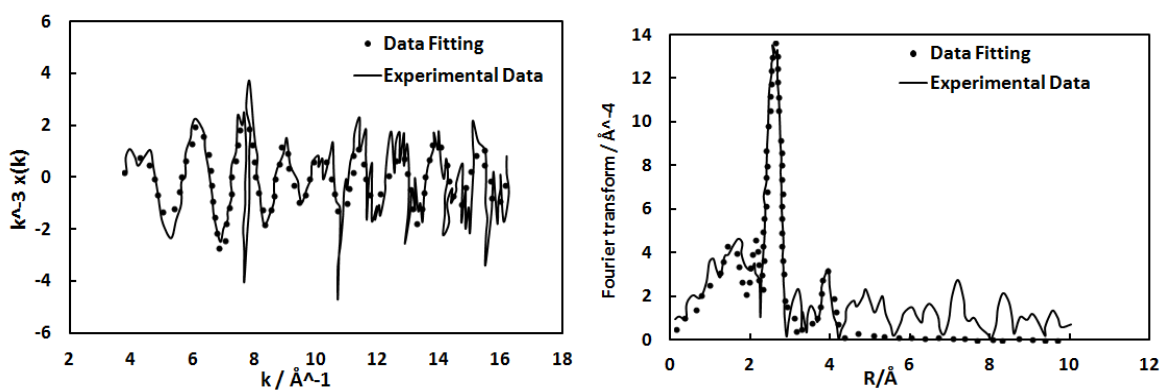
303 On the other hand, Pt²⁺ ions in smaller cages are possibly migrating back to the zeolite supercages at relatively
304 high reduction temperatures. The adducting ability of Fe ion may contribute to the contraction of Pt–Pt
305 bonding distance by higher Pt and Fe binding energy resulting in the enhancement of Pt particle dispersion on
306 zeolite external/interior surface. It was found that in general the Pt particle size on zeolite (i.e. 15PtFeancr3
307 and 15PtFeancr4) is relatively small in the presence of Fe²⁺/Fe³⁺, compared with 1.5 wt% Pt loading on zeolite
308 without Fe ion incorporated sample (i.e 15Ptancr4).



309

310

(a) Sample 15PtFeancr3 in O₂



311

312

313

(b) Sample 15PtFeancr4 in O₂

314 Figure 4: Comparison of EXAFS experimental raw data (in solid lines) and the fitted data (in dotted symbols) for
 315 1.5 wt% Pt loading Pt-Fe Y zeolite catalysts in O₂ purged gas cell with phase correction. The EXAFS data was
 316 collected at Pt L_{III} edge. (a) Sample 15PtFeancr3 - calcined at 350 °C and reduced at 300 °C (i.e. 15PtFeancr3);
 317 (b) Sample 15PtFeancr4 - calcined at 350 °C and reduced at 400 °C (i.e. 15PtFeancr4).

318 Table 3. The EXAFS data fitting results, collected at Pt L_{III} edge in O₂ purged gas cell at room temperature for
 319 sample 15PtFeancr3 and sample 15PtFeancr4, respectively.

15PtFeancr3	Shell 1 - O	Shell 2 - Pt	Shell 3 - Fe
N	0.92	1.26	0.54
R (Å)	1.99	2.57	2.59

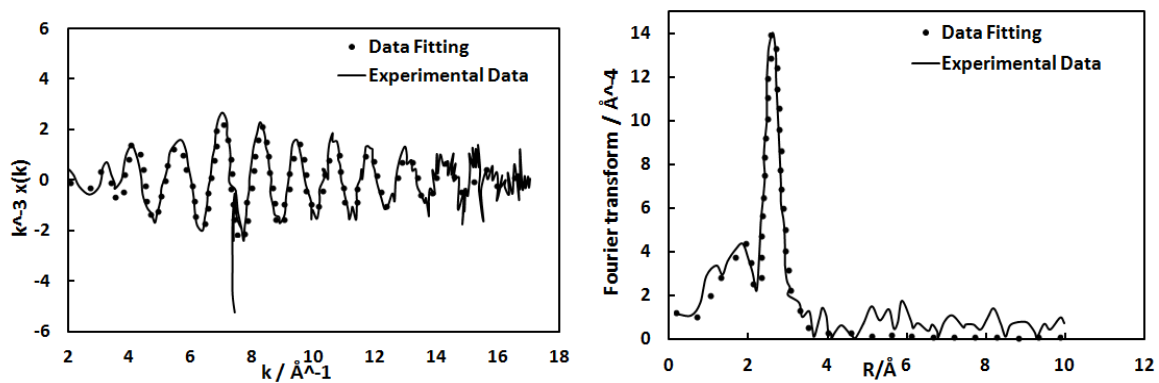
320

15PtFeancr4	Shell 1 - O	Shell 2 - Pt	Shell 3 - Fe	Shell 4 -Pt
N	0.75	1.55	0.65	1.00
R (Å)	1.94	2.56	2.44	3.99

321

322 3.2.2.2 Analysis of ex-situ EXAFS data at the Pt L_{III} edge in hydrogen gas at room temperature

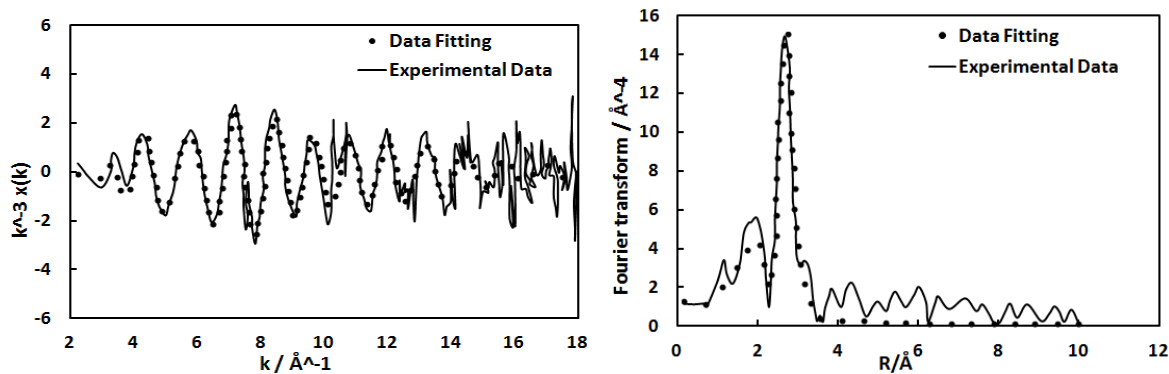
323 The Pt structure was analysed using EXAFS data collected at Pt L_{III} edge in hydrogen at room temperature. The
324 improvement of EXAFS (Chi) data noise level is clearly visible with no Pt-O bond predicted, indicating a
325 significant reduction of Pt samples in hydrogen. The breaking up of Pt-O bond could be due to the replacement
326 of oxygen by Fe to form a new Pt-Fe bimetallic bond. The second shell of Pt was predicted with a coordination
327 number of 3.82 for Fe incorporated sample with 1.5wt% Pt loading on zeolite, which was calcined at 350 °C
328 and reduced at 300 °C (i.e 15PtFeancr3) or 400 °C (i.e 15PtFeancr4), as illustrated in Figure 5. The
329 corresponding Pt-Pt bonding distance was determined at 2.71Å and 2.70Å, respectively (see Table 4). The Pt-Pt
330 bonding distances are slightly shortened while compared with the Pt metallic bonding distance of 2.75Å and
331 also those observed in 1.5 wt% Pt loading Y zeolite system with no Fe presence (i.e. 15Ptancr4). The Fe local
332 coordination number in the first shell was estimated to be 1.35 for sample 15PtFeancr3 and 1.51 for sample
333 15PtFeancr4 with associated Pt-Fe bonding distances of 2.62Å and 2.59Å, respectively. It can be seen that the
334 Fe particle size increases with the increase in reduction temperature. Also no oxygen atom was predicted,
335 which indicates that the Fe-Pt bimetallic particles were fully reduced in Hydrogen, and that the shortening of
336 Pt-Pt bonding distance may be due to the increase of Pt binding energy and the Pt atom electron deficiency as
337 a result of by metal particle polarization.



338

339

(a) Sample 15PtFeancr3 in hydrogen



340

341

(b) Sample 15PtFeancr4 in hydrogen

342 Figure 5. EXAFS data fitting for 1.5 wt% Pt loading Pt on Fe incorporated Y Zeolite catalysts in hydrogen with
 343 phase correction. The experimental data are presented in solid lines and the fitted data shown in dotted
 344 symbols, respectively. The EXAFS data was collected at Pt L_{III} edge. (a) Sample 15PtFeancr3 - calcined at 350 °C
 345 and reduced at 300 °C; (b) Sample 15PtFeancr4 - calcined at 350 °C and reduced at 400 °C.

346

347 Table 4. EXAFS data fitting results for data collected at Pt L_{III} edge in hydrogen gas at room temperature
 348 corresponding to sample 15PtFeancr3 and sample 15PtFeancr4, respectively.

15PtFeancr3	Shell 1 - Fe	Shell 2 - Pt
N	1.35	3.82
R (Å)	2.62	2.71

349

15PtFeancr4	Shell 1 - Fe	Shell 2 - Pt
N	1.51	3.82
R (Å)	2.59	2.70

350

351

352

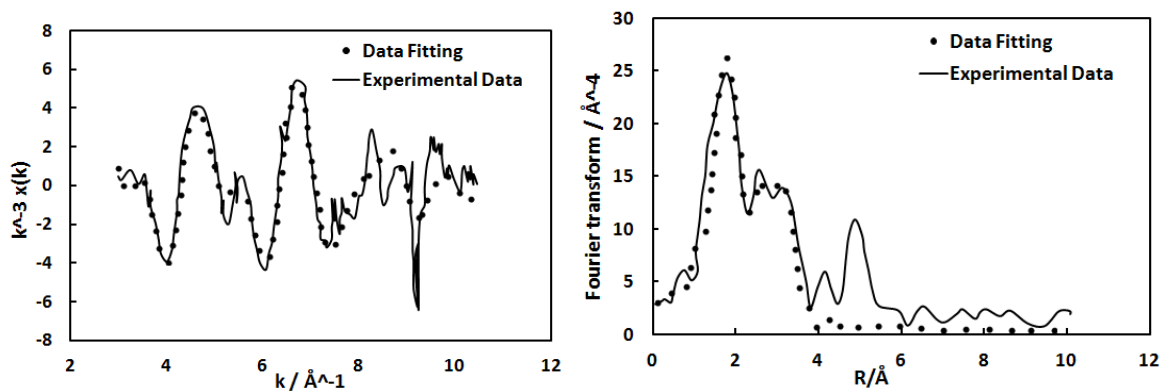
353

354 3.2.2.3 The ex-situ EXAFS data analysis for sample collected at Fe K-edge in O_2 gas at room
 355 temperature

356 The analysis continues for EXAFS data collected at Fe K-edge in order to restate evidences found at Pt L_{III} edge
 357 and to determine the metallic Fe-Pt oxides. The oxygen atom coordination number in shell 1 is predicted as
 358 2.04 for sample 15PtFeancr3 and 1.4 for sample 15PtFeancr4, and the associated Fe-O distance is 1.95Å and
 359 1.91Å, respectively. An extra 'O' coordination number was found in shell 4 with coordination number of 4.35

360 for 15PtFeancr3 and 3.24 for 15PtFeancr4, respectively indicating strong oxidation of Pt-Fe metal alloy. A
 361 significant increase in the Fe-Fe coordination number is predicted at 0.92 (compared to 0.54 at Pt L_{III} edge) for
 362 sample 15PtFeancr3 and 1.27 (compared to 0.65 at Pt L_{III} edge) for sample 15PtFeancr4 with the increased
 363 inter-atomic distance of 2.45Å (vs 2.59Å at Pt L_{III} edge) and 2.38Å (vs 2.44Å at Pt L_{III} edge). The Pt coordination
 364 number was predicted to be 0.95 (vs 1.26 at Pt L_{III} edge) and 1.90 (vs 2.55 at Pt L_{III} edge) for Fe associated Pt
 365 samples in comparison. The discrepancy of coordination number and inter-atomic distance between fitted
 366 EXAFS data collected at Pt L_{III} edge and at Fe K-edge may be attributed by the noise level in EXAFS raw data.
 367 The significant shortening of Fe bonding distance compared to that of a standard Fe-Fe bonding distance of
 368 2.65Å is probably caused by differences in the atom charge density between Pt and Fe. However, no major
 369 contraction of Pt bonding distance was found.

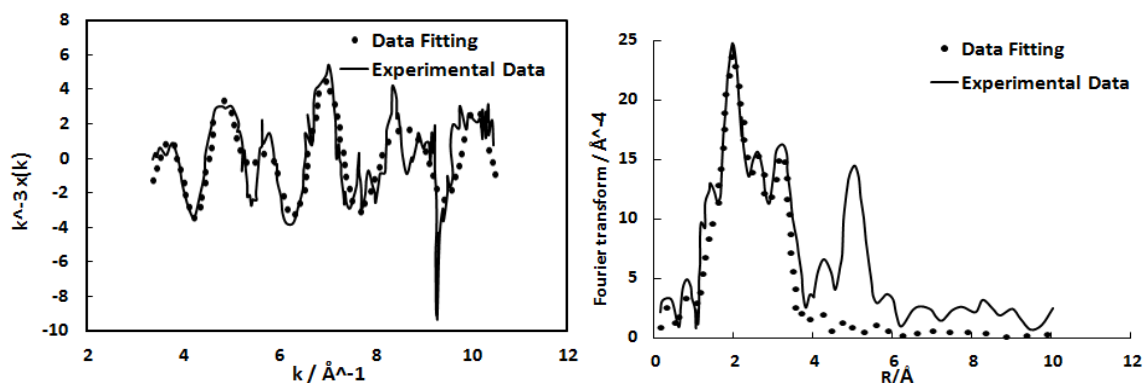
370



371

372

(a) Sample 15PtFeancr3 in O₂



373

374

(b) Sample 15PtFeancr4 in O₂

375 Figure 6. EXAFS data fitting for 1.5 wt% Pt-Fe/Y zeolite electrocatalyst samples in O₂ with phase correction. The
 376 experimental data are displayed in solid lines and the fitted data presented in dotted symbols, respectively.
 377 The EXAFS data was collected at Fe K-edge. (a) 15PtFeancr3 - 1.5 wt% Pt loading on Fe incorporated Y zeolite

378 calcined at 350 °C and reduced at 300 °C; (b) 15PtFeancr4 - 1.5 wt% Pt loading on Fe incorporated Y zeolite
379 calcined at 350 °C and reduced at 400 °C.

380

381 Table 5. EXAFS Data fitting results, data collected at Fe K-edge in O₂ gas at room temperature for samples
382 15PtFeancr3 and 15PtFeancr4, respectively.

15PtFeancr3	Shell 1 - O	Shell 2 - Fe	Shell 3 - Pt	Shell 4 - O
N	2.04	0.92	0.95	4.35
R (Å)	1.95	2.45	2.72	3.36

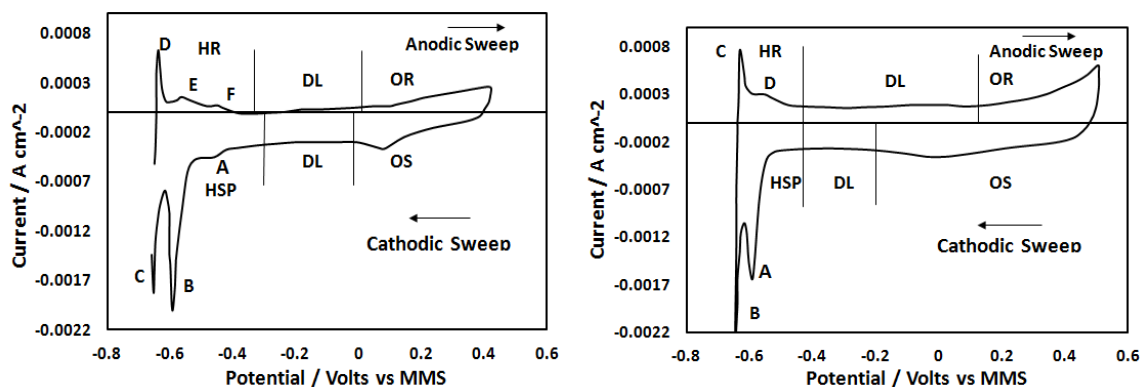
383

15PtFeancr4	Shell 1 - O	Shell 2 - Fe	Shell 3 - Pt	Shell 4 - O
N	1.40	1.27	1.90	4.84
R (Å)	1.91	2.38	2.72	3.24

384

385 3.3 The cyclic voltammetry (CV) measurement

386 The cyclic voltammetry (CV) measurement was performed in an electrochemical cell to determine the electro-
387 activity of species in the electrolyte solution using Nafion[®] bound electrode made by the mixture of Fe
388 incorporated Pt electrocatalyst on Y zeolite and carbon powder. The response of an electrochemical reaction
389 was determined by monitoring current change with potential. The CV measurement of a 1.5 wt% Pt loading on
390 Pt/Y zeolite carbon | Nafion[®] electrode (i.e. 15Ptancr4) and a 1.5 wt% Pt/C | Nafion[®] electrode (i.e. 15Pt/XC-
391 72R) made from a commercially available 40wt% Pt/XC-72R carbon catalyst mixed with the extra XC-72R
392 carbon, is depicted in Figures 7a-7b, to investigate the hydrogen adsorption/desorption activity on Pt surface
393 at -0.65 V in 2.5 mol dm⁻³ H₂SO₄ solution.



394

395

(a)

(b)

396 Figure 7. The steady state CV curves are measured at a scan rate of 1 mV/s in 2.5 mol dm⁻³ H₂SO₄ solution. (a)
 397 1.5 wt% Pt/XC-72R electrode prepared by a mixture of 40 wt% Pt/XC-72R with extra plain XC-72R carbon
 398 powder (i.e. 15Pt/XC-72R), (b) 1.5 wt% Pt/Y zeolite (i.e. 15Ptancr4) made with extra plain XC-72R carbon
 399 powder.

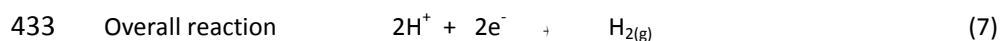
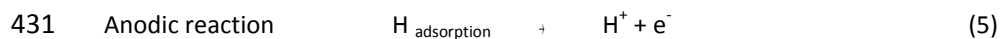
400

401 The CV lines consist of three distinguished regions, namely hydride region comprising hydrogen adsorption
 402 (HSP) and hydrogen reduction (HR) regions; oxide reduction (OR) and oxide Stripping (OS) regions; and the
 403 double layer region (DL), respectively. For the 1.5 wt% Pt/XC-72R electrode (i.e. 15Pt/XC-72R) (as seen in
 404 Figure 7a), the hydrogen adsorption potential (HSP) of the hydride region starts at -0.32 V and goes down to -
 405 0.65 V, where a strong adsorption of H⁺ ions occurs at the peak 'B'. This is attributed by the high H₂ adsorption
 406 energy on the plane of the Pt and also electron conduction between Pt and Pt, with the peak 'C' being
 407 responsible for a hydrogen evolution at -0.65V. The peak 'A' is linked with the weakly adsorbed H⁺ ions forming
 408 covalent bonds on Pt catalytic sites. The H re-oxidation of the peak 'D' is observed in the anodic sweep of
 409 potential from -0.65 V to -0.36 V, and the peaks 'E' and 'F' represents weakly and strongly bound H desorption
 410 sites, respectively. A current increase at the potential oxidation region (OR) of 0.12 V to 0.5 V indicates the
 411 formation of Pt oxide species at Pt electrode surface, while an oxide stripping (OS) occurs at the cathodic
 412 sweep in a potential region of 0.5 V to -0.02 V. A charger separation between the Pt metal surface and the
 413 electrolyte solution was predicted to occur in a double layer (DL) region from 0.02 V to -0.36 V and -0.36 V to
 414 0.12 V in a reverse sweep manner.

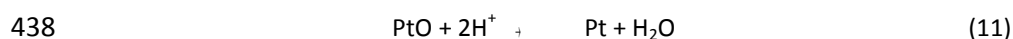
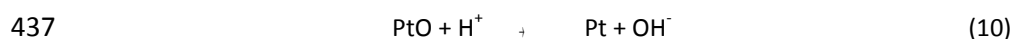
415 Figure 7b displays a typical CV of 1.5 wt% Pt/Y Zeolite carbon mixed Nafion[®] bound working electrode (i.e.
 416 15Ptancr4), with the electrochemical oxidation and reduction features similar to that on 1.5 wt% Pt/XC-72R

417 Nafion[®] bound electrode. The potential sweep region was confined between -0.65 V and 0.5 V at a slow sweep
 418 rate of 1 mV/s. The Pt nano-particles electrochemical activity was predicted to occur in the hydride region
 419 between -0.45 V and -0.65 V in both cathodic and anodic sweep directions. Hydrogen adsorption peak,
 420 representing a strong Pt bounded catalytic site (peak 'A'), has been observed at -0.6 V, and no weakly bounded
 421 Pt catalytic site was determined. It is possible that both weakly and strongly bounded hydrogen may adsorb
 422 similar amount of energy, resulting in difficulties to distinguish them unless a much slower sweep rate, e.g. less
 423 than 1 mV/s, being used. Further decrease in potential to -0.65 V leads to hydrogen evolution, as illustrated by
 424 (peak 'B'). The re-oxidation of hydrogen (peak 'C') was determined at -0.64 V, and sole hydrogen desorption
 425 peak 'D' was detected at -0.56 V. An oxidation current in the anodic sweep was recorded in a potential range
 426 from 0.15 V to 0.5 V, and oxygen was stripped in a potential region of 0.5 V to -0.2 V in the direction of
 427 cathodic sweep. A small peak predicted at 0 V is probably due to the removal of Pt oxides.

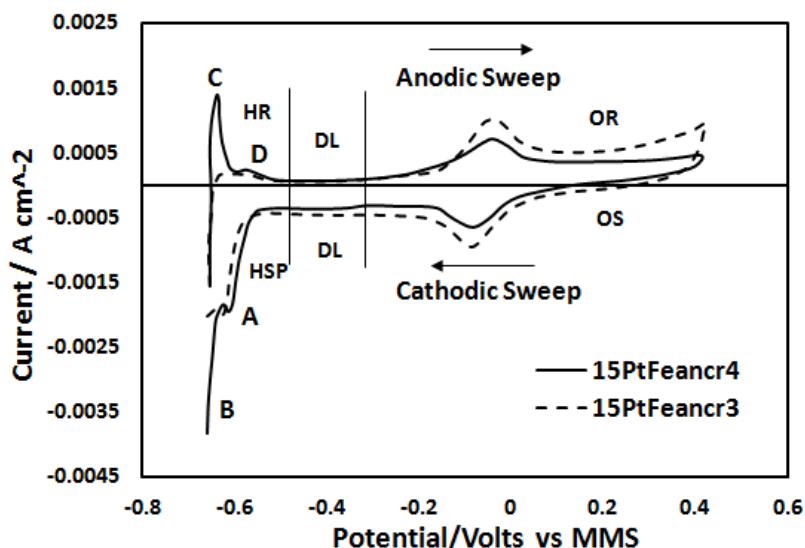
428 The electron transfer of hydrogen adsorption/desorption in the hydride region on Pt active site follows the
 429 reaction equations below:



434 The Pt surface oxidation/reduction due to H₂O is represented below:



439



440

441 Fig. 8. Steady state CVs are measured in a $2.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution at a scan rate of 1 mV/s . The dashed line
 442 represents the CV measurement for sample 15PtFeancr3, and the solid line is the CV measurement for sample
 443 15PtFeancr4.

444

445 Figure 8 depicts the electrocatalytic activity of $1.5 \text{ wt\% Pt-Fe/Y Zeolite | Nafion}^\circledast$ working electrode (i.e.
 446 15PtFeancr3 and 15PtFeancr4) at the potential region between $+0.5 \text{ V}$ and -0.65 V . The CV curve consists of
 447 very different electrochemical behaviour with only two distinguished regions associated with hydrogen
 448 adsorption/desorption peaks.

449 The current measurement of the double layer (DL) however is consistent in a potential region of -0.5 V to -0.35
 450 V . The values of two quasi-reversible peaks are determined at 0.2 V and 0.1 V , respectively, which indicates
 451 the electrochemical oxidation and reduction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion redox surface groups. The high oxidation current
 452 change (in dotted line) was measured by the electrode made by 15PtFeancr3 Y zeolite and the current
 453 increases in the positive potential region (OR) upon to 0.5 V . This is in good agreement with the EXAFS data
 454 regarding a high oxygen coordinate value around Pt for 15PtFeancr3. The oxide stripping (OS) occurs at 0.5 V
 455 to -0.2 V during the cathodic sweep of the potential. The large current drop (HSP) and the increase (HR) due to
 456 hydrogen adsorption (peak 'A') and hydrogen evaluation (peak 'B')/hydrogen re-oxidation (peak 'C') and
 457 desorption (peak 'D') in hydride region was predicted for the cell with an electrode made by 15PtFeancr4 (in
 458 solid line). This implies that Pt active sites are higher on electrocatalyst 15PtFeancr4 than that of 15PtFeancr3.
 459 The hydrogen re-oxidation and desorption current is significantly suppressed on an electrode made by

460 15PtFeancr3, and there is no clear hydrogen re-oxidation and desorption peaks detected. This may be due to
461 similar energy levels of these two sites. The Fe incorporated 1.5 wt% Pt electrocatalyst shows consistent
462 tendency for electrochemical activity, compared with 1.5 wt% Pt/Y zeolite sample (i.e. 15Ptancr4) or 1.5 wt%
463 Pt/XC-72R electrocatalyst made by 40 wt% Pt/XC-72R and extra carbon powder mixture, respectively.

464 The hydrogen adsorption/desorption peak in hydride region demonstrated the presence of electron/ion
465 transfer at the interface of Nafion[®] bound Pt or Pt-Fe zeolite electrode and electrolyte solution. However, Pt
466 electrocatalytic performance depends on Pt particle size and their distribution on zeolite at different thermal
467 treatment conditions. The high Pt active sites were dedicated for sample treated at high reduction
468 temperature (i.e. 15PtFeancr4), compared with sample 15PtFeancr3 treated at relatively low reduction
469 temperature. Based on previous studies of Gallezot et al. [16, 21], the location of Pt²⁺, Fe²⁺ and Fe³⁺ ions on
470 zeolite depends on the calcination/reduction temperature and metal zeolite surface interaction. The Pt ions
471 are likely to occupy small cages, such as sodalite cages and hexagonal prisms at the calcination temperature of
472 350+ °C. The high negative charge density of small cavities may provide a main driving force to move the
473 multivalent metal ions from supercages to sodalite cages, in particular to the hexagonal prisms [30]. On the
474 other hand, Pt particles can more easily migrate backward to the supercages at reduction temperature of 400
475 °C instead of temperature of 300 °C. The small cages can be blocked in the presence of Fe³⁺ during calcination
476 owing to high positive charge density, while the Fe²⁺ ion in the supercages acts to anchor the Pt particles onto
477 the zeolite cage wall [31].

478 From the study of hydrogen 'spillover' pathway on Pt/C catalyst by Srinivas and Rao [32], it was proposed that
479 the hydrogen adsorption/desorption occurs on carbon based Pt active sites. Later study by McBreen [33]
480 further revealed the current generation on Pt active sites, which are situated remotely from the conducting
481 material surface with fast surface mobility of adsorbed species on the electrode. Therefore, the surface active
482 sites of Pt particles that are not in direct contact with solid conductive polymer electrolytes such as the
483 Nafion[®] membrane can involve in an interfacial process through the pathway of surface conductance.

484 Zeolite material is generally known as an electrical insulator, but it is capable of acting as a solution like ionic
485 conduction [34] and as an electron bank to donate or receive electrons in the presence of the zeolite
486 Brønsted or Lewis acidic sites to produce a flow of protons along zeolite acidic sites. This results in two

487 possible pathways in contribution to the electronic conducting in 1.5 wt% Pt or Pt-Fe bimetallic alloy/Y Zeolite
488 carbon powder | Nafion[®] electrode system, either the surface mobility of adsorbed species or hydrogen
489 adatoms/H⁺ ion 'spillover' through zeolite framework or on electrode surface [19]. The study of Wen et al. [19]
490 indicates that a hydrogen atom 'spillover' process on Pt/C electrode can occur during the surface diffusion
491 process, in which hydrogen ions (H⁺) were able to form OH group with carbon acidic surface oxides where the
492 carbon black was a main substrate of the electrode surface. The study by Fujimoto [35] has revealed H⁺
493 'spillover' in gas phase on Brønsted and Lewis acidic sites where there is a catalytic reaction to take place.
494 Similar process might be adopted to explain the electrochemical conductivity in Pt/Y zeolite or Pt-Fe bimetallic
495 alloy/Y zeolite electrode system, despite that zeolite is an electrical insulator. The Brønsted sites on zeolite
496 and phenolic group on carbon materials contain acidic sites/groups, which can be ionized to provide protons
497 and to contribute to the surface conductance.

498 A 'spillover' pathway may occur during the surface diffusion process of the adsorbed species [18]. The H⁺
499 'spillover' can be transmitted between active sites and along the zeolite substrate surface to increase the
500 surface conductivity of the electrode. In this case, water has played an important role to facilitate hydrogen
501 migration into the Pt catalytic sites on the zeolite framework. Hence, the H⁺/hydrogen 'spillover' provides a
502 direct pathway for Pt particle that are not in direct contact with Nafion[®] to participate in the electrochemical
503 reaction at the catalyst | Nafion[®] interface, and in further strengthening the surface conductivity. The cyclic
504 voltammetry measurement has confirmed that a reversible hydrogen adsorption/desorption peak can be
505 detected in 1.5 wt% Pt-Fe bimetallic alloy/Y zeolite catalysts | Nafion[®] electrode system, in agreement with
506 that in well studied Pt/C electrode system. For surface oxygen containing species in 1.5 wt% Pt-Fe/Y zeolite
507 carbon mixed electrode | Nafion[®] system, the interfacial electrochemical reaction mainly involves ionic
508 conduction and surface conductivity. Therefore, the effect of ohmic drop is significant. Moreover, the electron
509 transfer may take place between the electrode and solution via free species, such as H⁺ and H₃O⁺. Ions are
510 transported through the free species by hitching a ride on water during their migration through the small
511 zeolite channels.

512

513

514 3.4 In-situ EXAFS study for 1.5 wt% Pt/Y zeolite and 1.5 wt% Pt-Fe/Y zeolite electrocatalysts

515 3.4.1 Pt particle structure study for 1.5 wt% Pt/Y zeolite electrocatalyst

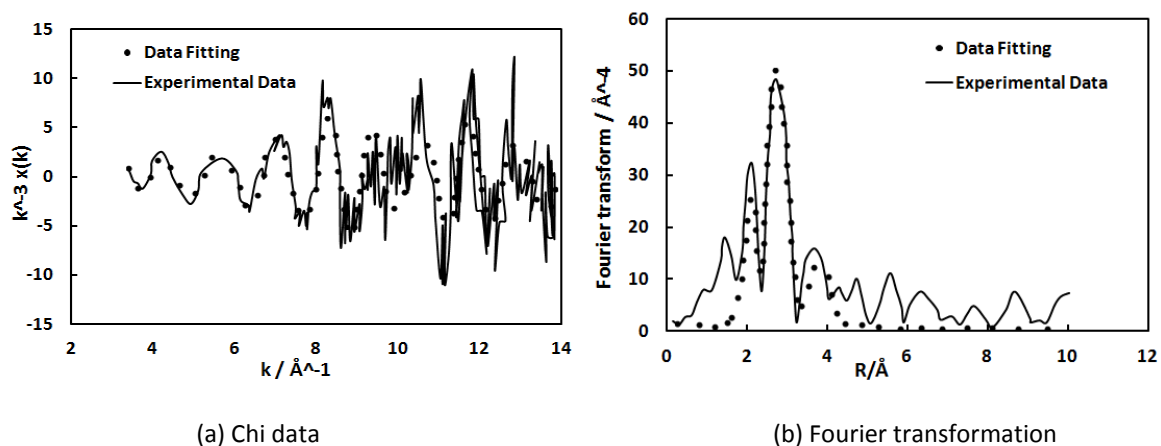
516 Figure 9 illustrates the EXAFS data fitting with the raw Chi data spectra ($k^3\chi(k)$ vs $k/\text{\AA}$) and Fourier transform
517 for 1.5 wt% Pt/Y zeolite (i.e. 15Ptancr4) electrocatalyst with correspondent to the fitting results illustrated in
518 Table 6. The in-situ EXAFS data was collected at Pt L_{III} edge at room temperature under the potential
519 deposition of -0.65 V in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. The curve fitting (in dotted lines) matches the general
520 form of the raw data (in dashed lines) very well and the data fitting was extended up to 3 shells with shell 1
521 and shell 2 predicted for Pt and shell 3 for oxygen, respectively. The Pt coordination numbers in shell 1 and
522 shell 2 are approximately 7.45 and 2.05. The introduction of third Pt-O shell data has significantly improved the
523 data fitting quality. A metallic nature of Pt nano-particle is determined with Pt-Pt distance of 2.77\AA , which
524 implies the preservation of the bulk of Pt characteristics. The in-situ prediction of Pt-Pt distance in 1.0 mol dm^{-3}
525 H_2SO_4 electrolyte solution is similar to that fitted using ex-situ EXAFS data collected in hydrogen gas cell. As the
526 Pt particle size is small, compared with fitting results for data collected in air and hydrogen gas cells, the Pt-O
527 bond may attribute to either the re-oxidation of Pt at -0.65 V in hydride region or the direct link of Pt
528 associated with oxygen on the Lewis acidic site.

529

530 Table 6. The data fitting results for 1.5wt% Pt/Y zeolite (i.e. 15Ptancr4) electrocatalyst under potential
531 deposition of -0.65 V in hydride region in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution.

15Ptancr4	Shell 1 - Pt	Shell 2 - Pt	Shell 3 - O
N	7.45	2.05	0.75
R/ \AA	2.77	3.85	2.19

532



533

534

535 Figure 9. EXAFS data fitting for 1.5 wt% Pt Y zeolite catalysts with phase correction (i.e. 15Ptancr4). The
 536 experimental data and the fitting results are presented in solid lines and dotted symbols, respectively. Data is
 537 collected at a potential of -0.65 V vs MMS reference electrode in 1.0 mol dm⁻³ H₂SO₄ solution under potential
 538 deposition. The EXAFS data was collected at Pt L_{III} edge.

539

540 3.4.2 Pt particle structure study for Fe incorporated 1.5 wt% Pt loading on Y zeolite

541 The Fe incorporated Pt particle structure on zeolite is characterised by using in-situ EXAFS technique, in which
 542 EXAFS data was collected at the Pt L_{III} edge with 1.5 wt% Pt loading on Y zeolite incorporated with Fe ions (i.e.
 543 15PtFeancr3 and 15PtFeancr4) under a potential deposition of -0.65 V in 1.0 mol dm⁻³ H₂SO₄ electrolyte
 544 solution. Figure 10 depicts the fitted EXAFS spectra and the corresponding data are presented in Table 7. The
 545 sample 15PtFeancr3 has shown poorer data fitting quality than that of sample 15PtFeancr4. The local Pt
 546 coordination number of shell 1 for sample 15PtFeancr3 is approximately 4.87, slightly lower than 5.07
 547 predicted for sample PtFeancr4. The Fe coordination number fitted in shell 2 is 1.96 for sample 15PtFeancr4
 548 and 1.37 for sample 15PtFeancr3, respectively. The average atom numbers of Pt particle in the hydride region
 549 has shown a significant increase with a decrease of Pt-Pt (2.72Å) and Pt-Fe (2.53Å or 2.51 Å) bonding
 550 distance compared to the Pt-Pt and Pt-Fe distances of 2.75Å and 2.59Å determined by previous en-situ EXAFS
 551 data analysis. The shortening of Pt and Fe bonding distance is possibly attributed to high electron deficiency of
 552 metal during charger transfer under a potential deposition process at -0.65 V. The fitting results in the hydride
 553 region indicate a high distribution of Pt particle for 1.5 wt% Pt loading Fe Y zeolite electrocatalyst system
 554 reduced at 400 °C (i.e. 15PtFeancr4), compared with electrocatalyst reduced at 300 °C (i.e. 15PtFeancr3). The
 555 high current change in hydride region observed by cyclic voltammetry measurement (as seen in figure 8) has

556 demonstrated a high level of coverage of Pt active sites of zeolite for catalyst of 15PtFeancr4. The current
 557 change in hydrogen adsorption/desorption region for catalyst 15PtFeancr3 is relatively low, implying a low
 558 coverage of Pt active sites.

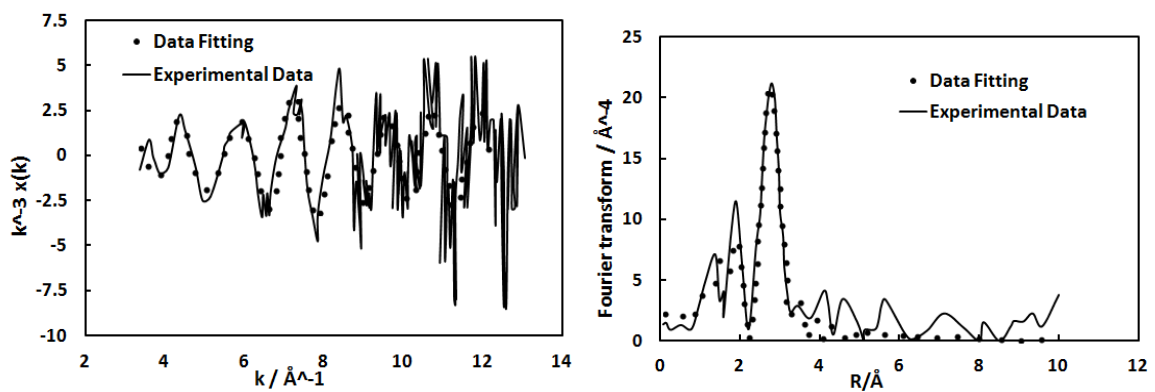
559 Table 7. EXAFS data fitting results for Fe incorporated Pt samples. Data were collected at Pt L_{III} edge at -0.65 V
 560 under potential deposition in 1.0 mol dm⁻³ H₂SO₄ electrolyte solution.

15PtFeancr3	Shell 1 - Pt	Shell 2 - Fe
N	4.87	1.96
R (Å)	2.72	2.53

561

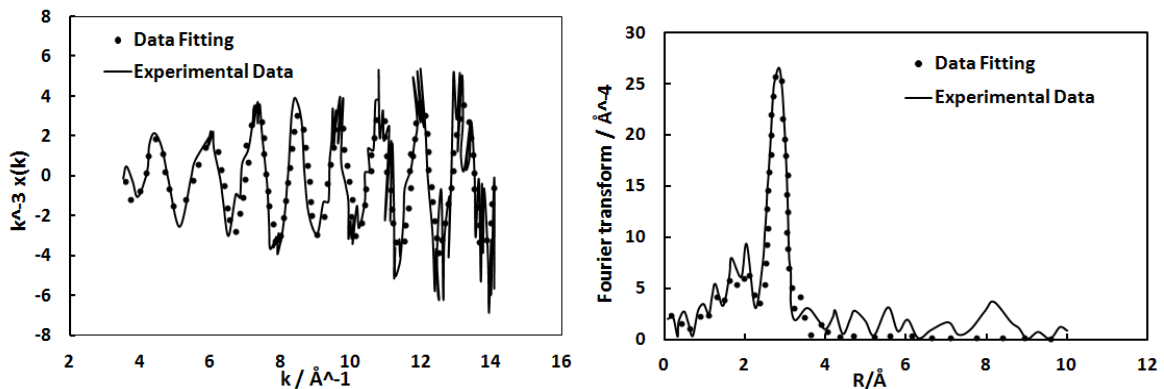
15PtFeancr4	Shell 1 - Pt	Shell 2 - Fe
N	5.03	1.37
R (Å)	2.72	2.51

562



563

564 (a) 15PtFeancr3 in 1.0 mol dm⁻³ H₂SO₄ solution



565

566 (b) 15PtFeancr4 in 1.0 mol dm⁻³ H₂SO₄ solution

567 Figure 10. EXAFS data fitting for 1.5 wt% Pt-Fe/Y zeolite catalysts with phase correction. The experimental data
 568 and the fitted results are presented in solid lines and dotted symbols, respectively. Data is collected at a
 569 potential of -0.65 V vs MMS reference electrode under potential deposition. (a) 15PtFeancr3 - 1.5 wt% Pt
 570 loading on Y zeolite incorporated with Fe calcined at 350 °C and reduced at 300 °C; (b) 15PtFeancr4 - 1.5 wt%
 571 Pt loading on Y zeolite incorporated with Fe calcined at 350 °C and reduced at 400 °C.

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 573
 574

4. Pt distribution on zeolite

575 4.1 Estimation of Pt particle size and Pt distribution

576 Based on the Benfield theory [26], the Pt cluster size and geometry can be estimated using the mean value of
 577 the first nearest neighboring coordination number \overline{N}_i of atoms in a cluster, as a function of cluster edge
 578 length. The formula for \overline{N}_i is derived from two geometric models, i.e. icosahedron and cubo-octahedron. It is
 579 assumed that Pt structure for Pt zeolite catalysts has an icosahedral model, as illustrated in figure 11. This is
 580 because an icosahedral cluster might be more metallic than that of cubo-octahedral model with same atom
 581 numbers. Subsequently, the total number of atoms N_{total} in a cluster and the average first – nearest
 582 neighboring coordination number \overline{N}_i can be calculated numerically using following formulae, based on the
 583 number of Pt shells in a cluster:

$$584 \quad N_{total} = (1/3)(2m - 1)(5m^2 - 5m + 3) \quad (12)$$

$$585 \quad \overline{N}_i = 6[(m - 1)(20m^2 - 25m + 12)] / [(2m - 1)(5m^2 - 5m + 3)] \quad (13)$$

587 where m represents the complete Pt shell number.

588

589 Table 8 illustrates the number of Pt atoms and the average first nearest neighboring coordination number in a
 590 Pt cluster for Pt zeolite catalysts in hydrogen reduction.

591 For Fe incorporated Pt zeolite, a simplified formula can be used to calculate mean coordination number \overline{N}_i of a
 592 cluster containing Pt and Fe atoms follows equation 14 below.

$$593 \quad \overline{N}_i = \overline{N}_i(Pt - Pt) + \overline{N}_i(Pt - Fe) \quad (14)$$

594
 595
 596

Table 8. Pt atoms mean first nearest neighboring coordination number in a Pt cluster.

Acronym Name	Catalyst 15Ptancr4	Catalyst 15PtFeancr3	Catalyst 15PtFeancr4
\overline{N}_i from refinement - Pt	6.33	5.17	5.33

597

598

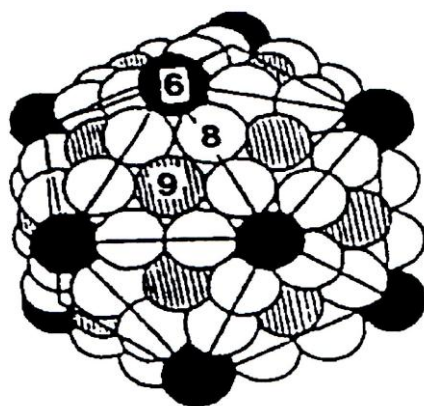
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604 Figure 11: The icosahedrons structure with 147 atoms ($m = 4$), where atom 6 represents the vertex atom with
 605 6-coordinate, atom 8 shows the edge atom with 8-coordinate, atom 9 represents the atom with 9-coordinate
 606 in the triangular face [26].

607

608 The Pt particle size is estimated at 0.7 nm for 1.5 wt% Pt loading on zeolite with 55 atoms in Fe incorporated
 609 samples (i.e. 15PtFeancr3 and 15PtFeancr4) and at 1 - 1.1 nm for 1.5 wt% Pt loading on zeolite with 147 atoms
 610 in a Pt cluster. Previous cyclic voltammetric measurement has shown a high surface area distribution of Pt for
 611 Fe incorporated Pt zeolite catalyst, indicating a highly dispersed Pt particle surface area on zeolite due to the
 612 presence of Fe^{2+} ions. As Sachtler et al. suggested [12], Fe^{2+} cation in zeolite channel can be oxidized to Fe^{3+}
 613 during the calcination process, as Fe^{3+} ions are more likely to migrate into zeolite small cages (i.e. sodalite
 614 cages and hexagonal prisms) due to high charge density. The mobility of Pt ions can be restrained by Fe^{2+} ions
 615 in supercages and zeolite external surface as a result of anchoring Pt on the zeolite cage wall.

616 4.2 Pt active surface area and distribution on electrode surface

617 The actual Pt loading can be calculated by following equations, in which the edge jump is obtained from EXAFS
 618 data subtraction.

619
$$\ln(I / I_0) = \mu x \quad , \quad (15)$$

620
$$m = (\mu x) * (S) / (\mu / \rho) \quad , \quad (16)$$

621 where μ is the total linear absorption coefficient (cm^{-1}) for the primary beam, defined by the natural log of the
 622 ratio of the transmitted photon intensity (I) and incident intensity (I_0). χ is the thickness of the material. m is

623 total mass of the element interested and S is cross sectional surface area of the pellet or electrode. ρ is the
624 density of the absorbance. The mass absorption coefficient μ/ρ is known to be 179 for Pt at the L_{III} edge at
625 room temperature, and S is 1.327 cm^2 .

626 The surface area of Pt particle in direct contact with H_2SO_4 solution can be determined by applying hydrogen
627 adsorption/desorption peak measurement. Table 9 illustrates the comparison of Pt distribution on zeolite for
628 Pt-Fe bimetallic alloy and Pt zeolite catalysts treated at different reduction temperatures.

629 The Fe incorporated Pt zeolite catalyst reduced at $400 \text{ }^\circ\text{C}$ (i.e. 15PtFeancr4) has a significantly high Pt surface
630 area. This has been demonstrated by analyzing the hydrogen adsorption peak due to current charge transfer in
631 the hydride region at the potential between -0.65 V and 0 V . The Pt active surface area is measured at 84.98
632 m^2/g for the Fe incorporated Pt zeolite catalyst reduced at $400 \text{ }^\circ\text{C}$ (i.e. 15PtFeancr4) with $1.54 \text{ wt} \%$ Pt loading
633 on zeolite. The Fe incorporated Pt zeolite catalyst reduced at $300 \text{ }^\circ\text{C}$ (i.e. 15PtFeancr3) gives a consistent Pt
634 active surface area, compared with the Pt loading on zeolite catalyst reduced at $400 \text{ }^\circ\text{C}$ (i.e. 15Ptancr4). The Pt
635 active surface area is predicted at $55.9 \text{ m}^2/\text{g}$ with $1.49 \text{ wt} \%$ Pt loading on zeolite for Fe incorporated sample
636 15PtFeancr3, and $51.29 \text{ m}^2/\text{g}$ with $1.52 \text{ wt} \%$ Pt loading for Pt alone sample 15Ptancr4, respectively. The
637 prepared Pt loading on zeolite for all samples studied is consistent with the proposed value of $1.5 \text{ wt} \%$ Pt
638 loading on Y zeolite.

639 The net Pt atoms per cm^2 predicted for samples 15PtFeancr4, 15Ptancr4 and 15PtFeancr3 are in an order of
640 $5.28 \times 10^{17} > 5.21 \times 10^{17} > 5.11 \times 10^{17}$ per cm^2 , respectively. The slightly low number of Pt net atom per cm^2 for
641 sample 15PtFeancr3 may be associated with relatively low Pt loading on zeolite. In general, Pt surface atoms
642 decrease with the decrease of reduction temperature. However, it seems that the Fe incorporated Pt catalyst
643 has resulted in better Pt surface atom dispersion at high reduction temperature, compared to Pt loading with
644 no Fe incorporated zeolite catalyst treated at same condition. The Pt surface atom dispersion for Fe
645 incorporated Pt zeolite sample reduced at $400 \text{ }^\circ\text{C}$ (i.e. 15PtFeancr4) is predicted to be 24.70% , which is
646 significantly higher than that of 16.30% and 14.66% for Fe incorporated Pt zeolite catalyst reduced at $300 \text{ }^\circ\text{C}$
647 (i.e. 15PtFeancr3) and Pt zeolite catalyst reduced at $400 \text{ }^\circ\text{C}$ without Fe incorporated (i.e. 15Ptancr4). The
648 associated Pt surface atoms per cm^2 on zeolite were determined to be 13.04×10^{16} (i.e. 15PtFeancr4), 8.33

649 $\times 10^{16}$ (i.e. 15PtFeancr3) and 7.64×10^{16} (i.e. 15Ptancr4), respectively. The data indicates a high Pt surface area
 650 distribution of 15PtFeancr4, due to relatively small Pt particle size.

651 The present study has shown that Pt distribution in zeolite system is mainly influenced by Fe ions and chemical
 652 reduction temperature. A highly dispersed Pt on zeolite can be achieved at high reduction temperature in H_2
 653 and result in the formation of Pt and Fe bimetallic bond. The high Pt active surface area that leads to high
 654 electrocatalytic activity has been demonstrated by the cyclic voltammetry measurement in $2.5 \text{ mol dm}^{-3} H_2SO_4$
 655 electrolyte solution by Nafion[®] bound Pt-Fe electrode.

656 Table 9. Pt active surface area m^2 per gram and the value of Pt atom distribution in the per cm^2 electrode area.

Catalyst	15Ptancr4	15PtFeancr3	15PtFeancr4
Pt active surface area m^2/g	51.29	55.9	84.98
Calculated mass quantity in wt %	1.52	1.49	1.54
N_T Pt atoms per cm^2 ($\times 10^{17}$)	5.21	5.11	5.28
N_S Pt surface atoms per cm^2 ($\times 10^{16}$)	7.64	8.33	13.04
Dispersion N_S/N_T (%)	14.66	16.30	24.70

657
 658 * N_T : total atoms in a cluster; N_S from Benfield theory (i.e. total number of surface atoms in a cluster for
 659 samples 15PtFeancr3 and 15PtFeancr4 are 12.)

660
 661 A shell-type distribution of Pt particles can be used to understand Pt and Fe dispersion on zeolite for catalyst
 662 15PtFeancr4 reduced at $400^\circ C$. In this case, Fe^{2+} ion acts in a very similar way as H^+ ion to promote the Pt
 663 particle distribution by anchoring Pt on zeolite surface/supercage wall and further to restrict Pt migrations
 664 through zeolite microchannel at H_2 reduction temperature of $400^\circ C$. While the collapse of zeolite
 665 microstructures, about 50% decrease of zeolite surface area for Fe incorporated Pt zeolite catalysts could be
 666 possible due to the Fe species blockage of the zeolite opening pores, and this agrees well with other published
 667 observations [12]. Subsequently, some of Pt particles can be encapsulated in zeolite cages. The in-situ EXAFS
 668 data analysis (see, e.g. figure 10 and table 7) has predicted a relatively high Fe atoms distribution close to Pt
 669 first shell for catalyst 15PtFeancr3 pre-treated in H_2 gas cell at reduction temperature of $300^\circ C$. In this case, Fe

670 has failed to produce a high Pt distribution based on CV measurement of hydrogen coverage of surface area.
671 Both Pt and Fe are more likely encaged inside the zeolite microchannel.. The reduction temperature of 300 °C
672 is not high enough to enforce Pt and Fe migration back to either zeolite surface or supercage. This leads to the
673 incompleteness of reduction of Pt in H₂, unless further increasing the reduction temperature until 400 °C i.e. like
674 case of catalyst 15PtFeancr4.

675

676 5. Conclusion

677 In this paper, we studied the characteristics of zeolite supported Pt-Fe bimetallic nano-particle and their
678 electrocatalytic performance using EXAFS data analysis and cyclic voltammetry measurements. The electron
679 transfer pathway at small metal particles was also investigated under electrochemical control.

680

681 The resultant analysis has led to the proposal of the electron transfer pathways, illustrating the Pt-Fe bimetallic
682 electrocatalytic activity and their electronic conduction via 1.5 wt% Pt loading Pt-Fe/Y zeolite carbon powder |
683 Nafion[®] bound electrode system. The formation of a mixed Fe oxide phase can prevent metal surface mobility
684 of Pt and lead to increase in Pt distribution of zeolite. A further increase in Pt stability is possible on the
685 formation of the Pt and zeolite oxide interface. It was suggested that Fe²⁺ could act as a proton to anchor Pt on
686 zeolite cage wall and restrain the mobility of Pt on zeolite in chemical reduction process. The strong interaction
687 between Fe²⁺ and zeolite substrate can stabilize the Pt on zeolite surface and prevent the sintering of Pt metal
688 particles at high temperature, leading to a highly dispersed Pt surface area distribution, which is achieved by
689 controlling chemical reduction temperature in H₂ gas cell during calcination and reduction process. Both in-situ
690 EXAFS and cyclic voltammetry measurements indicate that Pt particle has a relatively higher surface area
691 distribution for Pt-Fe zeolite catalysts reduced at 400 °C in H₂ gas cell (i.e. 15PtFeancr4) than that of Pt zeolite
692 (i.e. 15Ptancr4) or Pt-Fe zeolite electrocatalysts reduced at 300 °C (i.e. 15PtFeancr3) with a better
693 electrocatalytic performance in hydride region. In general, Pt surface area is high for Pt-Fe zeolite
694 electrocatalyst, compared to that of Pt zeolite electrocatalyst.

695

696 The Fe³⁺ ions oxidized from Fe²⁺ were favourably located inside the zeolite small cages to block the zeolite
697 channel. A high Pt particle distribution is predicted for Fe incorporated Pt sample reduced at 400 °C (sample
698 15PtFeance4). The Pt-Pt bonding distance is 2.75Å - 2.77Å, indicating the metallic characteristics of the bulk Pt.

699

700 The Pt particle size on zeolite with Fe incorporated catalyst is relatively small, compared with catalyst without
701 adding a secondary Fe metal. This is evidenced by cyclic voltammetry measurement for hydrogen
702 adsorption/desorption peak in the hydride region via current charge transfer. It was suggested that the H⁺ ions
703 'spillover' pathway could be used to depict the electron transfer and Pt electrocatalytic performance in
704 electrolyte solution. The presence of hydrogen species adsorbed on Pt might contribute to either direct
705 electron transfer or the mobility of H_{ads}/H⁺ species. Alternatively, ionic and electronic conduction may also
706 occur via free species, such as H⁺ and H₃O⁺ through which ion is transported by hitching a ride on water during
707 their migration through zeolite channels to increase the electrode surface conductivity.

708

709 Conclusively, this study has confirmed that Pt nano-particles in Y zeolite system can be electrochemically
710 accessed on Nafion[®] bound electrode made by Pt zeolite or Pt-Fe zeolite despite the DC insulation of zeolite.
711 The Pt electrocatalytic performance can be improved by adding a secondary metal such as Fe element. The
712 cyclic voltammetry and EXAFS measurements also show chemical oxidation and reduction temperature is
713 crucial to achieve high Pt dispersion on zeolite. Conclusively, Fe incorporated Pt catalyst as a new type of
714 electrocatalyst exhibits some promises for fuel cell applications to reduce the cost as well as to enhance the
715 fuel cell efficiency.

716

717 6. References

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