

Investigation of zeolite supported platinum electrocatalyst for electrochemical oxidation of small organic species

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Highlights

- Pt ion exchange with Y type zeolite and calcination and reduction.
- H⁺ spillover at electrode and solution interface and through zeolite framework.
- Pt particle size measurement by EXAFS.
- Pt electrocatalytic performance by CV measurement.
- Electro-oxidation of small organic species on Pt surface.

Abstract: Zeolite supported Pt electrocatalysts, made by ion exchange method using Pt/Y type zeolite, have been investigated to determine Pt electrochemical activity of HCOOH and CH₃OH oxidation using the cyclic voltammetry (CV) and the extended X-ray adsorption fine structure (EXAFS) techniques. The study reveals that the introduction of excess H⁺ ions during electrocatalyst pre-treatment could enhance electrochemical reaction on Pt surface due to higher Pt dispersion, regardless of zeolite being a direct current electronic conducting insulator. Two possible conduction pathways might contribute to the electrocatalytic reaction on Pt surface with Pt particle size and loading: (1) hydrogen atoms/H⁺ ions spillover through zeolite framework and at the electrode and solution interface; (2) surface mobility of adsorbed species on electrode surface. The water may act as a carrier in assisting the migration of the H⁺ ions throughout zeolite channels to facilitate the charger and electron transfer in such an electrical system.

Keywords: Pt on Y zeolite, H⁺ spillover species surface mobility, HCOOH and CH₃OH oxidation, CV, EXAFS.

1. Introduction

Carbon supported platinum (Pt/C) as a common type of electrocatalyst has been widely used in direct methanol fuel cell (DMFC) applications with Pt loading on carbon normally in a range of 20% - 40%, which is prohibitively expensive. Furthermore, the Pt/C electrocatalysts can contain large-size

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33 Pt particles that may decrease the electrocatalytic activity. Previous study by Min et al. [1] revealed
34 the increase of specific activities with the decrease of the surface area for carbon supported Pt
35 electrocatalyst, in which the oxygen reduction on Pt surface was a structure-sensitive reaction
36 associated with the adsorption strength of oxygen intermediate on the Pt surface. Hence,
37 considerable research efforts have been made in the past decades by developing a highly dispersed
38 nanostructured Pt electrocatalyst to improve fuel cell efficiency and economic viability for energy
39 applications.

40 Zeolite can provide an environment to produce highly dispersed Pt metal particle, owing to its high
41 selectivity and great capacity of absorbing and retaining water by the creation of zeolite proton
42 conducting membranes for solution like ionic conduction through interconnecting channels without
43 damaging the zeolite crystalline lattice structure [2-4]. The growth of Pt particle on zeolite is mainly
44 controlled by O₂ calcination step in gas phase and high dispersion of Pt can be achieved by further H₂
45 reduction step [5]. A slow heating process at a high O₂ flowrate would be preferable to avoid Pt non-
46 uniform distribution on zeolite introduced by auto-reduction [6] that may produce large Pt metal
47 particles during the removal of ammonia ligands at 300 °C [7-9]. Pt is also found favourable to
48 remain in the zeolite supercage at 350 °C in O₂ and 400 °C in H₂, respectively, resulting in a particle
49 size of 0.6 – 1.3 nm, which is much smaller than that of graphene based materials with Pt particle
50 size growing up to 1.5 – 19 nm [10].

51 Pt was more stable at zeolite sodalite cage, mainly due to its strong polarization nature of the Pt-d
52 bond electron configuration [11]. A high degree of Pt dispersion was reported in the presence of H⁺
53 ions by forming Pt–H adduct in zeolite structure. H⁺ ions can act as a chemical anchor to diminish the
54 sintering of Pt particles at 400 °C in H₂. The polarization of Pt particles by the nearby cations, i.e. H⁺,
55 might result in the electron deficiency of Pt, leading to the change of Pt catalytic activity and
56 spectroscopic properties [12, 13]. Moreover, the charge transfer between Pt and nearby
57 neighbouring zeolite support oxygen atoms can play an important role during this process [14, 15].

58 The disorder of Pt particle on zeolite framework has had a dramatic effect on the Pt electronic
59 structure by the extended X-ray adsorption fine structure (EXAFS) [16, 17]. The Pt-Pt bond distance
60 was shortened to less than 2.75 Å than that of Pt bulk metal in the presence of strong charger
61 transfer between Pt clusters with the increase of the Pt-Pt binding energy due to Pt electron
62 deficiency [18], compared to Pt in a non-zeolite supported system, i.e. Pt/SiO₂. Vaarkamp et al. [19]
63 predicted an average Pt particle size consisting of approximately 15 atoms with the first shell
64 coordination number and Pt-Pt distance of 5.5 and 2.75 Å, respectively.

65 The electrochemical activity of Pt nanostructure on zeolite was previously investigated by Rolison et
66 al. [4]. The Pt was found to exhibit particular chemical and physical characteristics that could
67 enhance the electrochemical reaction, owing to high ionic strength between electrodes. Liu et al.
68 [20] suggested that hydrogen spillover is an important process to promote Pt electrocatalysis for
69 Pt/C electrode. The H⁺ ions adsorbed on the Pt active surface could spillover and diffuse into the
70 surface of the inert support to form acidic surface oxides for an interfacial reaction of
71 electrocatalytic process being taken place on Pt surface. The spillover of hydrogen has been
72 discovered in both Pt/Al₂O₃ and Pt/SiO₂ catalyst systems to promote the transport of an active
73 species between catalyst active sites. Zhang et al. [21] also observed hydrogen spillover from Pt to
74 zeolite Brønsted and Lewis acidic sites in gas phase.

Pt appears to be one of the best catalysts for dissociating the C-H bond at a relatively low potential [22], which is favourable to oxidise small organic species, such as, methanol (CH₃OH) and formic acid (HCOOH). However, past studies showed that the high electrocatalytic activity of Pt for methanol oxidation can be attributed by both high dispersion of redox-active Pt nanocrystal and active sites in high surface area of catalyst support, i.e. ZSM-5 zeolite [23]. Hsieh et al. [24] also discovered that Pt catalyst supported by material containing oxygen function groups, e.g. graphene oxides, is much more favourable for HCOOH oxidation, owing to strong interactions between metal ions and oxidised substrates, thus limiting the CO poison on Pt surface. El-Nagar and Mohammed [25] has drawn a similar conclusion about an oxygen atmosphere being important to facilitate CO oxidation at a low potential level.

Zeolite can offer high active sites interconnected by oxygen atom to enhance Pt dispersion and nucleation. However, the electrochemical oxidation and the reduction of CH₃OH and HCOOH species on zeolite supported Pt with regard to hydrogen spillover process at the Pt/Y zeolite electrode and solution interface have not yet been fully investigated, since zeolite lacks the direct current (DC) electronic conduction, and the electro-organic reaction on Pt surface is generally a slow process due to the restriction of high current density generation [26].

In this study, laboratory made 1.5 wt% and 5 wt% loading Pt electrocatalysts with or without excess H⁺ ions, introduced into zeolite structure by ion exchange method, will be investigated to determine the Pt electrochemical activity to oxidise CH₃OH and HCOOH species by cyclic voltammetry (CV). The Pt particle size and dispersion on zeolite will be characterised by EXAFS using a Nafion[®] bound electrode, fabricated by Pt/zeolite and carbon powder mixed with Nafion[®] to form ultra-thin film and membrane on electrode surface [2, 3]. The charger/electron transfer at electrode and solution interface will be investigated to understand Pt and zeolite conducting pathway, especially in the presence of excess H⁺ ion on zeolite.

99

100 2. Experimental

101 2.1. Pt/Y zeolite electrocatalysts ion exchanged using Pt(NH₃)₄(NO₃)₂ or Pt(NH₃)₄(NO₃)₂/NH₄NO₃ salts

102 The 1.5 wt% and 5 wt% Pt loading on Y zeolite electrocatalysts was made by ion exchange method
103 [17, 18] using Pt(NH₃)₄(NO₃)₂ salt (denoted as 15Ptancr4 for 1.5 wt% Pt loading and 5Ptancr4 for 5
104 wt% Pt loading on Y zeolite thereafter) or Pt(NH₃)₄(NO₃)₂/NH₄NO₃ salt (denoted as 15Ptanxcr4 for 1.5
105 wt% Pt loading and 5Ptanxcr4 for 5 wt% Pt loading on Y zeolite thereafter) in neutral solution,
106 respectively.

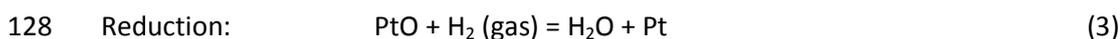
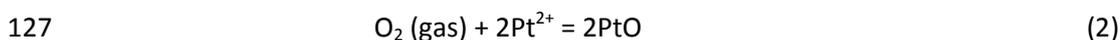
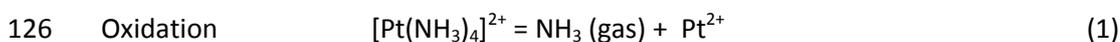
107 An appropriate quantity of Pt(NH₃)₄(NO₃)₂ was thoroughly dissolved in 200 ml of triply distilled
108 water. The ion exchange process was then taken place in water-jacketed reactor, where the sodium
109 Y zeolite powder was dispersed at a concentration of 1 g per 100 ml. The Pt ion was slowly added by
110 pumping Pt(NH₃)₄(NO₃)₂ salt solution into the reactor. The sample was then washed with triply
111 distilled water until no [Pt(NH₃)₄]²⁺ complex detected by Ultraviolet (UV) [27]. After washing, sample
112 was later dried overnight in an oven.

113 In case of the excess nitrate ion exchange method using $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2/\text{NH}_4\text{NO}_3$, the NH_4NO_3 was
114 added firstly into the suspended zeolite using stoichiometric titration method to provide a NH_4NO_3
115 concentration of $0.063 \text{ mol dm}^{-3}$ prior to the adding of the $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ salt.

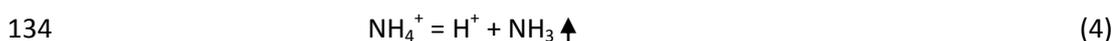
116 2.2. Calcination and Reduction

117 The synthesis of Pt nanostructures on Y zeolite was carried out by applying the calcination and
118 reduction procedure to remove the Pt co-ordinate ligand, i.e. a crucial chemical step associated to
119 the formation of Pt nano-particle dispersion on zeolite substrate [8].

120 $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ salt Y zeolite samples were purged with argon at a moderate temperature in a
121 fluidized bed reactor to dry out the water moisture. This will avoid the growth of large-size Pt
122 particles [9]. After cooling, O_2 gas was introduced into the reactor to re-heat samples up to 350°C .
123 Then, samples were chemically reduced at a temperature of 400°C by purging with 5% H_2 and 95%
124 N_2 gas mixture to produce a fine Pt distribution on zeolite. The following equations present the Pt
125 oxidation and reduction reactions [8]:



129 For sample ion exchanged with NH_4NO_3 salt (prior to the adding of the $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ salt), the
130 sample was heated at 300°C in argon to produce a fine distribution of the excess H^+ ions on zeolite
131 framework using the reaction in equation (4) below. The Pt oxidation and reduction reactions after
132 the introducing of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ions were followed by the same procedure presented in equations (1)
133 – (3) .



135

136 2.3. Electrochemical Cell and Cyclic Voltammetry

137 The electrode was made of electrocatalyst with 1.5 wt% and 5 wt% Pt loading on zeolite and
138 (untreated) XC-72R carbon powder mixture mixed with 15 wt% Nafion[®] solution (i.e. 5 wt% solution
139 in Aliphatic Alcohols and H_2O from Aldrich) as a binder. The resultant paste was then hot pressed on
140 a sheet of 9 cm^2 carbon paper (E-TEK TGHP-90) for solidification. A disc of 2.5 cm^2 diameter of
141 electrodes was then trimmed for CV measurement and a disc of 1.3 cm^2 for in-situ EXAFS
142 measurement.

143 The charge separation on electrode was investigated in a glass-jacketed electrochemical cell,
144 consisting of working electrode, $\text{Hg}/\text{Hg}_2\text{SO}_4$ Mercury/Mercuries Sulphate (MMS) reference electrode
145 and a Pt gauze counter electrode. The in-situ EXAFS measurement was carried out in an
146 electrochemical cell formed by two acrylic discs with two Kapton windows cut in the middle,
147 accomplished by a working electrode connected with a gold wire current collector to reinforce the
148 contact in the cell system via Pt gauze count electrode. The $\text{Hg}/\text{Hg}_2\text{SO}_4$ MMS reference electrode
149 was then connected to the electrochemical cell using a salt bridge, re-assembled to produce a

150 sufficiently large absorption edge. The electrolyte was 2.5 mol dm^{-3} sulphuric acid (H_2SO_4) solution
151 for the standard CV measurement and 1 mol dm^{-3} for the in-situ EXAFS measurement at a scan rate
152 of 1 mV s^{-1} in a potential region of -0.65 V to 0.5 V, respectively, in which no solvent and electrolyte
153 decomposition were detected [28].

154 For electro-oxidation reaction of HCOOH and CH_3OH species on Pt surface, the CV measurement was
155 taken at 1 mV s^{-1} in an electrochemical cell containing 2.5 mol dm^{-3} sulphuric acid (H_2SO_4) and 1 mol
156 dm^{-3} methanol or formic acid solution, until a clear and stable CV curve obtained.

157

158 *2.4. The Extended X-ray Adsorption Fine Structure Measurement*

159 EXAFS measurements were performed using a Synchrotron Radiation Source (SRS) at STFC Daresbury
160 Laboratory, UK. The wiggler beam line was operated at conditions of 2 GeV and 100 mA. High-order
161 harmonics that might affect the amplitude of EXAFS were removed using a double-crystal Si220
162 monochromator. The 50% detuning of harmonic beam using gas ion chambers filled with Ar, Xe or Kr
163 and He was used to locate the Pt L_{III} absorption edge. A Pt foil was used as a reference sample for
164 EXAFS data collection.

165 Data analysis was carried out using in-house software EXCURV 98. The inter-atomic distance, atom
166 number and the type of backscattering neighbours were determined using a method proposed by
167 Abruna [29].

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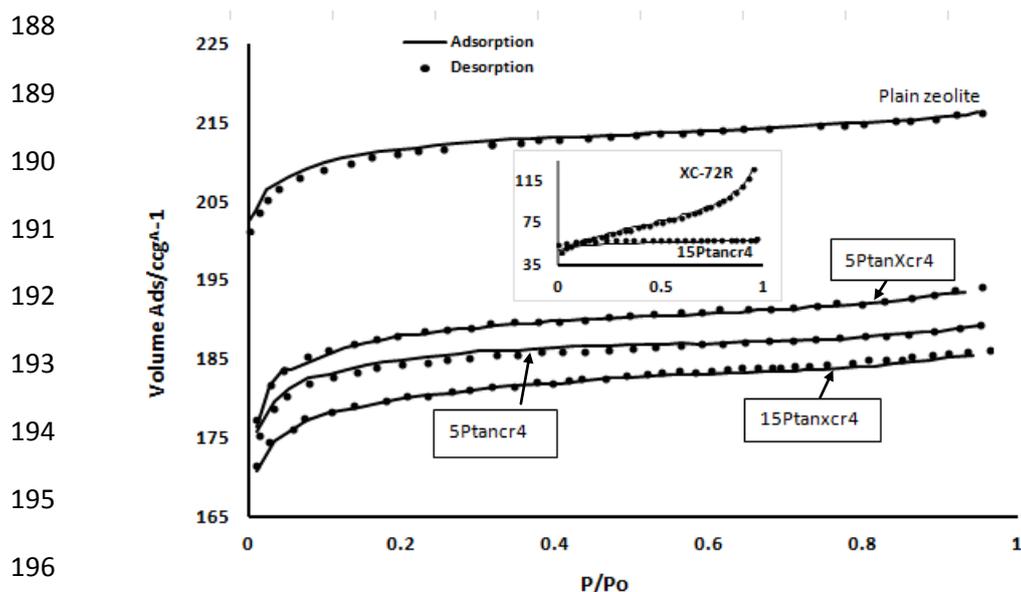
169 **3. Results and Discussion**

170 *3.1. Zeolite Brunauer-Emmett-Teller (BET) surface area measurement*

171 Figure 1 depicts the zeolite BET surface area measurement to investigate zeolite structure change,
172 owing to the calcination (O_2) and reduction (H_2) processes. The maximum 10% measurement
173 uncertainty given by sample 15Ptancr4 (i.e. at 168 m^2g^{-1}) (see in table 1) is mainly due to the
174 significant loss of zeolite crystal structure with merely 26.97% zeolite surface area preserved. The
175 plain zeolite sample has shown the highest surface area measured at 623 m^2g^{-1} . By comparing to
176 plain zeolite, it was found that about 86.52% of zeolite surface area was preserved by sample
177 15Ptanxcr4 (i.e. at 539 m^2g^{-1}), 90.37% and 88.76% by samples 5Ptanxcr4 (i.e. at 563 m^2g^{-1}) and
178 5Ptancr4 (i.e. at 553 m^2g^{-1}), respectively [30]. These data indicate that zeolite crystal structure is able
179 to be well-preserved in the presence of excess H^+ ions (e.g. sample 15Ptanxcr4 or 5Ptanxcr4) during
180 the calcination and reduction processes. The collapse of crystallized zeolite structure is found
181 predominant for 1.5% Pt loading sample 15Ptancr4 without H^+ ion presence, possibly owing to the
182 blockage of zeolite opening pores in small channels.

183 The surface area measured for XC-72R carbon powder is about 32.1% (i.e. at 200 m^2g^{-1}) compared to
184 that of plain zeolite, slightly higher than the value given by sample 15Ptancr4. The carbon powder is
185 only used as electrode binding paste in assisting to mix the Pt zeolite catalyst and Nafion[®] polymer
186 solution.

187



197 Fig. 1. Volumetric uptake of Nitrogen at a temperature of 77 Kelvin with adsorption in black solid
 198 lines and desorption in dotted symbols. All samples were made by calcination at 350 °C and
 199 reduction at 400 °C, respectively.

200 Table 1 BET Surface area measurement.

Sample	Plain zeolite	XC-72R	15PtanCr4	15PtanXcr4	5PtanCr4	5PtanXcr4
Surface area ($m^2 g^{-1}$)	623.2 ± 0.1%	200 ± 0.1%	168 ± 10%	539 ± 1.0%	553 ± 1.0%	563 ± 1.5%
Surface area preserved	100%	32.10%	26.97%	86.52%	88.76%	90.37%

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202 3.2. Cyclic Voltammetry measurement in H_2SO_4 electrolyte solution

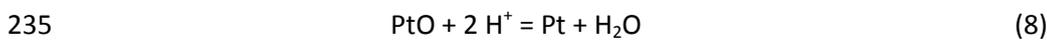
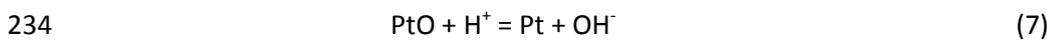
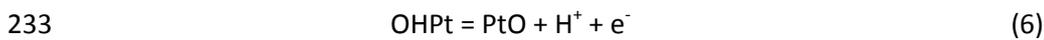
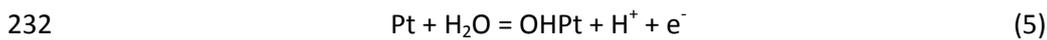
203 CV measurement was performed to determine the electro-activity of chemical species in the
 204 electrolyte solution on Pt surface by monitoring the current change against the potential. Figure 2
 205 depicts a comparison of electrochemical activity between -0.65 V and 0.5 V for samples 15PtanCr4,
 206 15PtanXcr4, 5PtanCr4 or 5PtanXcr4 Pt/Y zeolite | Nafion[®] bound working electrodes made by
 207 electrocatalyst with extra carbon powder mixture, respectively. The observed CV profile consists of
 208 very similar electrochemical behaviour with two distinguished hydrogen adsorption (HSP) and
 209 hydrogen reduction (HR) regions associated with the hydrogen adsorption peak (peak 'A'), hydrogen
 210 evaluation peak (peak 'B'), the re-oxidation peak (peak 'C') and desorption peak (peak 'D'),
 211 respectively.

212 A double layer (DL) current was measured at a potential range of -0.22 V to -0.40 V and -0.5 V to -
 213 0.33 V, during both cathodic and anodic sweeps. The current change in the hydride region provided
 214 by the electrode 15PtanXcr4 has seen significantly larger in terms of magnitude, with a well-resolved

215 hydrogen oxidation peak captured at -0.64 V. The electrode 15Ptancr4 predicted a hydrogen
 216 adsorption peak being further shifted towards a positive potential direction at -0.58 V, compared to -
 217 0.62 V and -0.61 V determined by those of 5Ptancr4 and 5Ptanxcr4, respectively. This indicated that
 218 the energy level of hydrogen adsorption on Pt active sites for the electrode 15Ptanxcr4 was
 219 relatively high. No visible feature of hydrogen desorption peak 'D' was observed by the electrode
 220 15Ptancr4, possibly due to very similar energy levels of these two sites, leading to insignificant
 221 oxidation and reduction redox surface group presence. The increase of hydrogen oxidation peak
 222 current was found to follow the order of samples as 15Ptanxcr4 -> 5Ptanxcr4 -> 5Ptancr4 ->
 223 15Ptancr4. There was a weak hydrogen desorption peak captured in the anodic sweep by the
 224 electrodes 5Ptanxcr4 and 5Ptancr4, consistent to that shown by the electrode 15Ptanxcr4.

225 The presence of electron transfer at the electrode and solution interface was evidenced by the
 226 hydrogen adsorption, evolution and desorption peaks in hydride region. It was known that Pt
 227 electrocatalytic performance was closely associated with Pt particle sizes and their distributions on
 228 zeolite [14], due to the polarization of Pt particles by neighbouring cations, i.e. H⁺, resulting in Pt
 229 electron deficiency. The significant hydrogen adsorption and evolution current change given by the
 230 electrode 15Ptanxcr4 has indicated the presence of high Pt distribution on zeolite.

231 Following equations describe an oxidation/reduction process on Pt surface:



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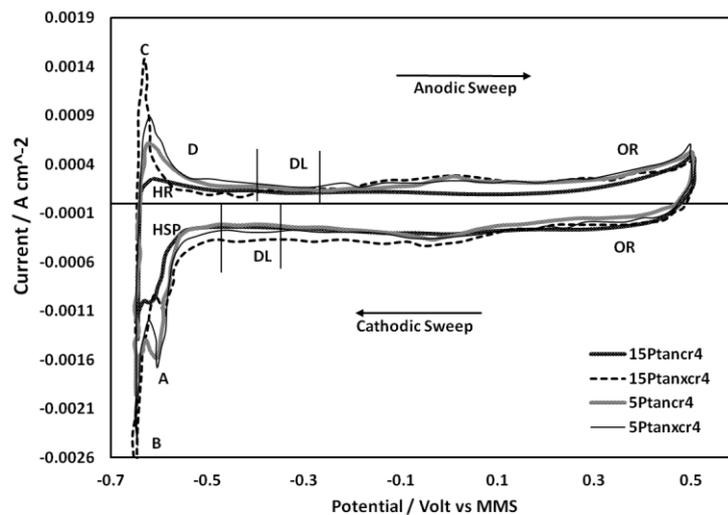
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246 Fig. 2. The CV measurement in 1.0 mol dm⁻³ H₂SO₄ solution for a potential range of -0.65 V to 0.5 V vs
 247 MMS reference electrode by the electrodes 15Ptanxcr4, 5Ptanxcr4, 15Ptancr4 and 5Ptancr4,
 248 respectively.

249 A dramatic arising of electrochemical activity was not observed by increasing Pt loading up to 5 wt%.
250 The current change at the hydride region for the electrode 15Ptanxcr4 is about 5.1 mA, compared to
251 that of 3 mA measured for the electrodes 15Ptanocr4 and 5Ptanocr4 or 5Ptanxcr4. The discrepancy
252 may be due to following two reasons given by the electrode 15Ptanxcr4: (1) the Pt distributions on
253 zeolite may have been increased; and (2) the Pt particle size is relatively small, resulting in an
254 increase of Pt surface area thus promoting Pt active sites [8, 11]. The formation of the Pt-H adduct in
255 zeolite structure can assist to diminish the sintering of Pt particle during calcinations process, due to
256 the increase of the Pt charge density. The hydrogen adsorption and desorption was found to take
257 place on Pt active sites via hydrogen 'spillover' pathway using carbon made Pt electrode [31], where
258 Pt not in direct contact with Nafion[®] membrane has been involved in an interfacial process through
259 surface conductance and surface diffusion process [20]. The H⁺ ions were able to form an OH group
260 with carbon acidic surface oxides. The electrochemical conductivity in the Pt/Y zeolite carbon
261 powder mixed | Nafion[®] electrode system might adopt a similar process of either the surface
262 mobility of adsorbed species or the hydrogen adatoms/H⁺ ions 'spillover' through the electrode
263 surface via ionic conduction of solution [3, 20]. Zeolite can act as an electron bank to donate or
264 receive electrons, resulting in a 'flow' of protons along acidic sites [32] for H⁺ ions being transmitted
265 between Pt active sites on zeolite.

266 The water was also found to have played a significant role in electrochemical reaction to migrate
267 hydrogen between Pt on zeolite framework by creating zeolite proton conducting membrane
268 strengthening electrode surface conductivity [3, 33]. The electrochemical reaction might involve a
269 charge/electron transfer at the electrode and solution interface in the presence of H⁺ and H₃O free
270 species, where ions are transferred by hitching a ride on water during their migration through zeolite
271 channels [3].

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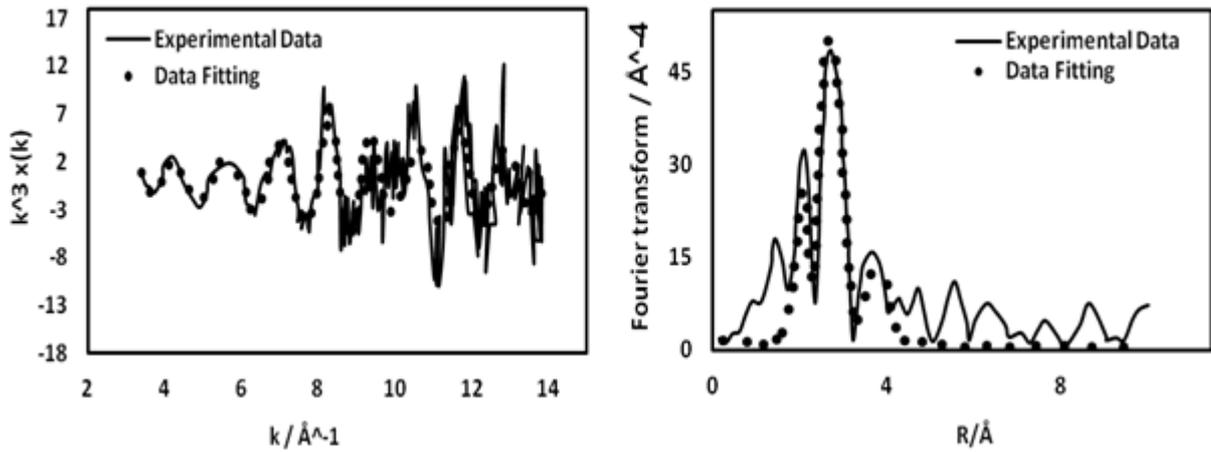
273 3.3. In-situ EXAFS study for 1.5 wt% and 5 wt% Pt/Y zeolite electrocatalysts

274 The in-situ EXAFS data was collected at the Pt L_{III} edge at room temperature under a potential
275 deposition of -0.65 V vs MMS reference electrode in 1.0 mol dm⁻³ H₂SO₄ solution. The data was then
276 fitted in R-space by k³ weighting and the EXAFS spectra were dominated by high Z-value neighbours
277 with phase correction using a computer code EXCURV 98 developed at Daresbury Laboratory, UK.

278 3.3.1. Pt particle analysis for Pt/Y zeolite electrocatalyst without excess H⁺ incorporated in zeolite 279 structure

280 Figure 3a illustrates the data fitting of the raw EXAFS Chi spectrum ($k^3\chi(k)$ vs $k/\text{Å}$) for electrode
281 15Ptanocr4 and their fitted results being presented in table 2. Some data scatterings were observed
282 in Chi spectrum at a slightly high noise level [30]. EXAFS data was subsequently fitted up to 3 shells
283 with a data fitting quality parameter called goodness fitting value (R_{exfd}) of 58% approximately. The
284 curve fitting (in dotted symbols) matches well against the raw data (in solid lines), with shells 1 and 2
285 Pt-Pt coordination numbers predicted at 7.45 and 2.0, respectively. The data fitting quality was
286 improved by adding a Pt-O shell. This might be attributed by Pt in direct contact with the zeolite
287 support oxygen. The Pt-Pt binding distance is determined at 2.77 Å, longer than a standard Pt-Pt
288 binding distance of 2.75 Å. This might be introduced by the re-oxidation of OH⁻ ions on the Pt active
289 sites, where the energy level is coherent to that required for the re-oxidation of OH⁻ ions.

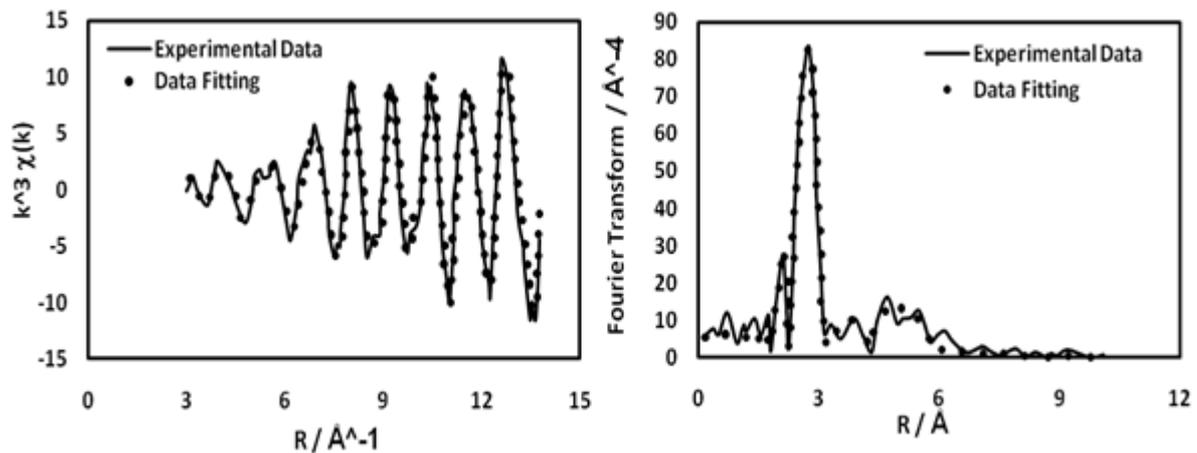
290 Figure 3b depicts the EXAFS spectra fitted for electrode 5Ptancr4. Up to four Pt shells were predicted
 291 with Pt coordination numbers of 6.78 at shell 1, 1.29 at shell 2, 3.10 at shell 3 and 6.3 at shell 4,
 292 respectively. The Pt-Pt binding distance is fitted at 2.76 Å. The increase of a Pt bond distance by 0.1
 293 Å is possibly due to the H adsorption on the Pt surface and hydrogen evaluation. It might also be
 294 associated with the interference of the negative charged zeolite support oxygen atom and Pt
 295 particles. No Pt neighbouring oxygen atom was detected; implying Pt particle is fully reduced at -
 296 0.65 V. The Pt particle size is estimated larger for 5 wt% Pt loading sample than those of 1.5 wt% Pt
 297 loading electrocatalysts predicted by Benfield theory [34] using icosahedrons or cubo-octahedron
 298 model.



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(a) 15Ptancr4



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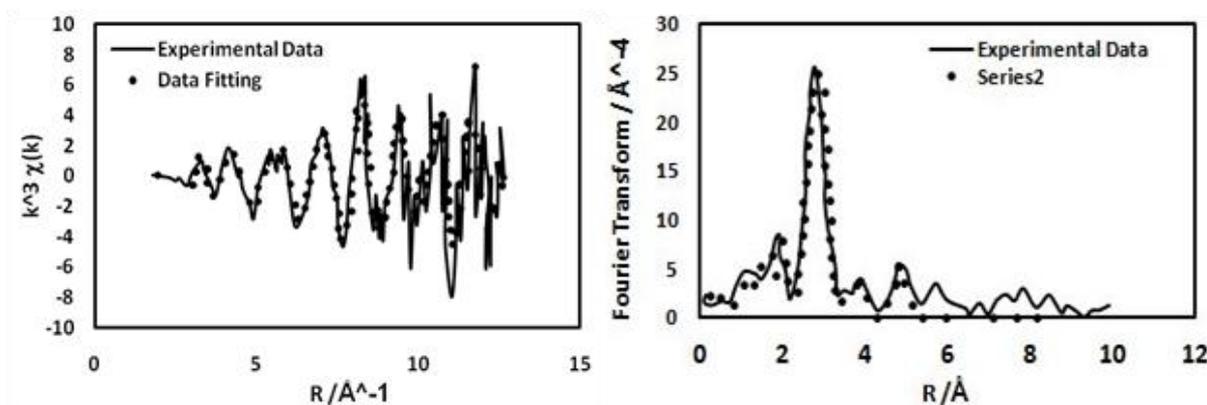
(b) 5Ptancr4

303 Fig. 3. EXAFS data fitted at the Pt L_{III} edge with phase correction. The experimental data and their
 304 fitting results are presented in solid lines and dotted symbols, respectively. Data were collected
 305 under a potential disposition at -0.65 V vs MMS reference electrode in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution.
 306 Samples: (a) 15Ptancr4; (b) 5Ptancr4, both without excess H^+ ions.

307 3.3.2. Pt particle analysis for Pt/Y zeolite electrocatalyst with excess H^+ ions incorporated in zeolite
 308 structure

309 Figure 4 shows EXAFS spectra fitting for electrocatalysts 15Ptanxcr4 and 5Ptanxcr4 decorated with
 310 excess H^+ ions on Y zeolite. A high noise level was shown in raw data of Chi spectrum by sample
 311 15Ptanxcr4, resulted in a slightly poor data quality [30]. The fitting results have been improved by
 312 adding the Pt-Pt third shell. This can be confirmed by the reduction of R_{exafs} value to 44.99%
 313 approximately. The Pt-Pt first shell coordination number is fitted at 6.38, and that of shells 2 & 3 are
 314 predicted at 1.48 and 5.15, respectively. The Pt-Pt binding distance is predicted at 2.77 Å, greater
 315 than 2.75 Å of sample 5Ptanxcr4, possibly attributed by the adsorption of hydrogen (H) on Pt surface
 316 or hydrogen evolution. No Pt-O shell was determined around Pt centre atom.

317 The goodness fitting value of R_{exafs} for sample 5Ptanxcr4 was predicted at 32.24%, approximately. Up
 318 to the fourth Pt-Pt shell was fitted with shell 1 Pt-Pt coordination number of 6.78, shell 2 at 1.29,
 319 shell 3 at 3.10 and shell 4 at 6.3, respectively. The Pt-Pt binding distance is 2.75 Å, indicating that Pt
 320 particle is metallic in nature to preserve the bulk Pt property.

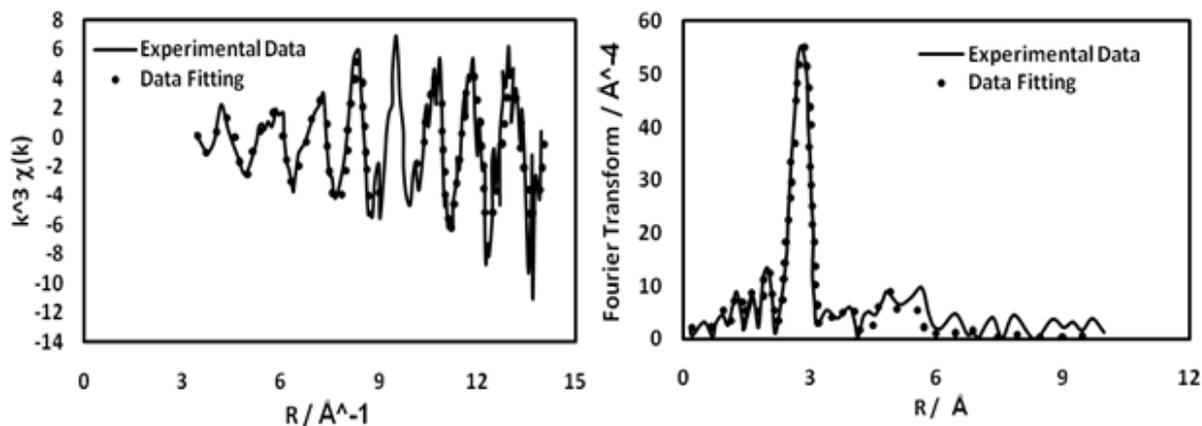


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(a) 15Ptanxcr4

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(b) 5Ptanxcr4

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326 Fig. 4. EXAFS data fitted at the Pt L_{III} edge with phase correction. The experimental data and their
 327 fitting results are presented in solid lines and dotted symbols, respectively. Data were collected
 328 under a potential deposition at -0.65 V vs MMS reference electrode in $1.0 \text{ mol dm}^{-3} H_2SO_4$ solution.
 329 Samples: (a) 15Ptanxcr4; (b) 5Ptanxcr4, both with excess H^+ ions.

330 Table 2 EXAFS data fitting results for 1.5 wt% and 5 wt% Pt loading Pt/Y zeolite electrocatalyst
 331 without excess H⁺ ions (i.e. 15Ptan_{cr}4, 5Ptan_{cr}4) or with excess H⁺ ions (i.e. 15Ptan_{xcr}4, 5Ptan_{xcr}4)
 332 in presence. The EXAFS data were collected under a potential deposition at -0.65 V in 1.0 mol dm⁻³
 333 H₂SO₄ solution at room temperature, respectively.

Samples		Shell 1 – O	Shell 2 – Pt	Shell 3 – Pt	Shell 4 – Pt	Shell 5 – Pt
15Ptan _{cr} 4	N	0.75	7.45	2.05		
	R(Å)	2.19	2.77	3.85		
5Ptan _{cr} 4	N		6.78	1.29	3.10	6.30
	R(Å)		2.76	3.89	4.78	5.43
15Ptan _{xcr} 4	N		6.38	1.48	5.15	
	R(Å)		2.77	3.90	4.80	
5Ptan _{xcr} 4	N		5.71	1.50	4.07	5.40
	R(Å)		2.75	3.87	4.77	5.40

334

335

336 3.3.3. The ex-situ EXAFS measurement

337 Although no additional Pt-Pt third shell is predicted for the electrode 15Ptan_{cr}4 by in-situ EXAFS
 338 measurement, this does not indicate that an average size of Pt is small owing to the presence of O
 339 neighbouring atom around the centre of Pt. This has been confirmed by the deterioration of the
 340 goodness fitting value of R_{exafs} at 58.87%, compared to that of 44.99% (R_{exafs}) determined for the
 341 electrode 15Ptan_{xcr}4. Subsequently, the ex-situ EXAFS analysis was carried out for a further
 342 investigation of Pt particle sizes and their distributions on zeolite.

343 Table 3 presents the fitting results of EXAFS data measured in H₂ gas cell using a mixture of 1.5 wt%
 344 or 5 wt% Pt/Y zeolite and boron nitride powder placed between two pieces of plastic film. There is
 345 no 'O' atom being predicted for 1.5 wt% Pt sample, indicating Pt might be fully reduced by H₂ gas. A
 346 Pt-Pt binding distance was measured to be 2.75 Å. The Pt fitting results for sample 15Ptan_{cr}4 are in
 347 good agreement with that given by Tzou et al. [35]. An average of Pt particle size consists of 17 Pt
 348 atoms, significantly higher than the value determined by in-situ measurement.

349 The number of Pt atoms determined by sample 15Ptan_{xcr}4 in H₂ gas cell consists of 13 atoms in a Pt
 350 particle, less than that in sample 15Ptan_{cr}4 under electrochemical reaction. This is possibly
 351 associated with the reduction of Pt thermal disorder in zeolite system with the increase of Pt binding
 352 energy by forming Pt metal proton adduct on zeolite acidic sites during the precursor thermal
 353 treatment process [36].

354 For 5 wt% Pt loading samples (i.e. 5Ptancr4 and 5Ptanxcr4) in H₂ gas phase, the Pt particle size is
 355 predicted slightly higher than those determined in electrolyte solution. The data fitting has shown an
 356 oxidation of sample 5Ptanxcr4 with O atom detected around the centre of Pt atoms. The Pt-O
 357 binding distance is significantly shortened from 2.2 Å to 1.93 Å, indicating the increase of an average
 358 Pt d-orbital binding energy with the increase of charge density on the zeolite support oxygen
 359 brought by charge compensation cations of H⁺ ions [14]. The Pt-Pt binding distance is determined at
 360 2.75 Å, again reflecting the metallic nature of Pt cluster.

361 Conclusively, a high level of Pt distributions on zeolite is acquired by samples, i.e. 15Ptanxct4 and
 362 5Ptanxcr4 with excess H⁺ ions presence. This has been demonstrated by hydrogen adsorption and
 363 desorption in hydride region.

364 Table 3 Data fitting results for 1.5 wt% and 5 wt% Pt/zeolite samples in H₂ gas at room temperature.

Samples		Shell 1 – O	Shell 1 – Pt	Shell 2 – Pt	Shell 3 – Pt	Shell 4 – Pt
15Ptancr4	N		6.33	0.88	3.34	6.40
	R(Å)		2.75	3.91	4.78	5.42
5Ptancr4	N		7.47	0.47	4.53	6.57
	R(Å)		2.75	3.88	4.79	5.45
15Ptanxcr4	N		6.00	1.59		
	R(Å)		2.75	3.90		
5Ptanxcr4	N	0.56	6.02	1.81	4.33	5.93
	R(Å)	1.93	2.75	3.89	4.78	5.42

365

366

367 3.4. Electrochemical oxidation of small organic species

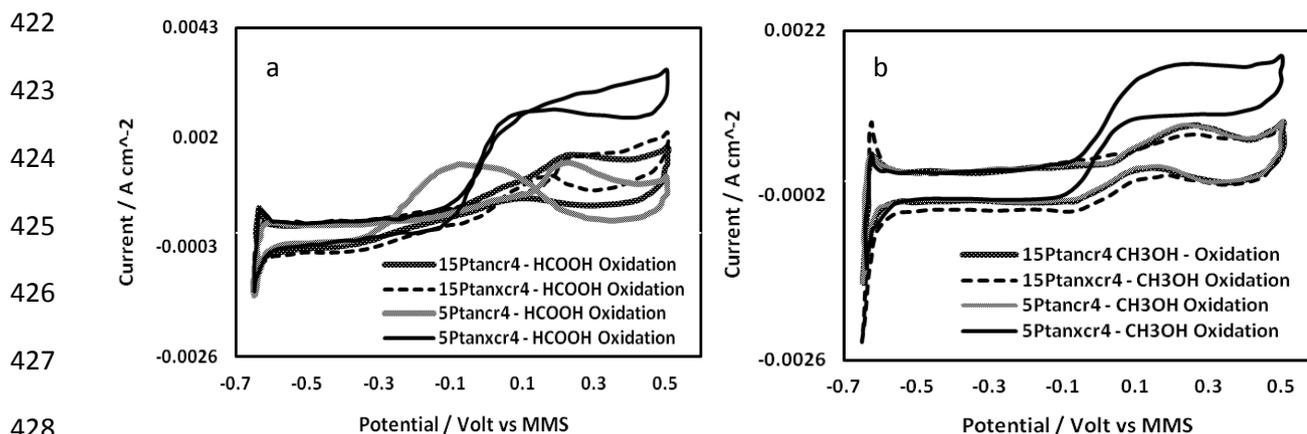
368 The oxidation behaviour of Pt/Y zeolite catalysts was determined by examining the electrooxidation
 369 of small organic species, i.e. CH₃OH and HCOOH, as Pt is considered to be the most suitable catalyst
 370 for electrooxidation of these small organic molecules [22, 37]. The accompanied by-product of
 371 carbon monoxide (CO) to poison Pt surface is examined by CV measurement in a mixture solution of
 372 2.5 mol dm⁻³ sulphuric acid (H₂SO₄) and 1 mol dm⁻³ of CH₃OH or HCOOH acid. The potential was
 373 cycled between -0.65 V and 0.5 V at a scan rate of 1 mV s⁻¹, until a clear and stable CV being
 374 obtained. The tendency of CV measurement for CH₃OH or HCOOH oxidation is generally in good
 375 agreement with that described in literatures [38-40].

376 Figure 5 displays the CV curves of HCOOH and CH₃OH oxidation on 1.5 wt% and 5 wt% Pt loading
 377 zeolite electrocatalysts, presenting a typical current change profile characteristics, which are found
 378 consistent to those provided by a commercial Pt/C electrocatalyst (i.e. Johnson Matthey) with a

379 particle size of 2.5 nm [38]. The HCOOH oxidation starts at a much negative potential region
 380 immediately after hydrogen desorption (see, e.g. figure 5a), compared to that determined in CH₃OH
 381 (see, e.g. figure 5b), indicating Pt surface is more favourable for HCOOH oxidation than that of
 382 CH₃OH. In general, the electrode made by sample 5Ptanxcr4 has shown a better performance to
 383 oxidise HCOOH and CH₃OH species. This was evidenced by a dramatic increase of
 384 oxidation/reduction current in both the cathodic and anodic sweeps, indicating that most of Pt
 385 active surface areas are free from CO occupation and thus available for electrochemical re-oxidation
 386 of HCOOH or CH₃OH [38, 39]. A more consistent CH₃OH oxidation/reduction current change was
 387 predicted by the electrodes of 15Ptanxcr4 or 15Ptanxcr4 and 5Ptanxcr4, respectively, whilst a small
 388 discrepancy of current change was determined by an oxidation of HCOOH. Their electrochemical
 389 activity follows a decreasing order of 5Ptanxcr4>5Ptanxcr4 > 15Ptanxcr4 > 15Ptanxcr5, respectively.
 390 The high electrocatalytic activity given by sample 5Ptanxcr4 may be associated with Pt oxidation (Pt-
 391 O) state on zeolite due to the interference of Pt with zeolite neighbouring active site, such as
 392 Brønsted site (see, e.g. descriptions in sections 3.3.2 and 3.3.3). Present study has shown the
 393 increase of Pt loading, i.e. from 1 wt% to 5 wt%, can promote the oxidation of HCOOH or CH₃OH, as
 394 seen in high current change, compared to that determined by a commercial Pt/C electrocatalyst at
 395 same scan rate of 1 mV s⁻¹ [38]. Kaur et al. [23] also observed a similar trend using Ce decorated
 396 ZSM-5 zeolite as support. This may be due to the attribution given by the interference of metal
 397 nanocrystal oxide and zeolite Brønsted acidity of high surface area zeolite, resulting in high stability
 398 of catalyst and high electrocatalytic activity [23]. The oxidation mechanism of HCOOH and CH₃OH on
 399 Pt electrodes was investigated by various research groups [23, 38-40] with similar conclusions. The
 400 final by-products given by electrochemical reaction were CO₂ and H₂O, accompanied by intermediate
 401 species of HCO and CO. The overall reactions for formic acid and methanol are presented below,
 402 respectively:



405 CO was found to be the main poison species involved in the oxidation of methanol and formic acid,
 406 resulting in the slowdown of the electrochemical reaction [38-41]. This has been reflected by
 407 inhibition of hydrogen adsorption/desorption region. In general, the formation of CO₂ by formic acid
 408 (HCOOH) oxidation is much more efficient than that determined for methanol (CH₃OH) [39, 42, 43],
 409 as evidenced by a high current yield between -0.3 V and 0.5 V (see, e.g. figure 5a). The present study
 410 indicates that both surface oxides and the available solution phase of OH⁻ ions could be the source of
 411 oxygen for the oxidation of CO, in agreement with those published findings [39, 44]. The overall fuel
 412 cell efficiency can be subsequently improved in formic acid, where the fuel crossover is much lower
 413 than that in methanol, owing to the repulsive interaction among the membrane sulfonic groups and
 414 anions [39]. The oxidation of small organic species appears to be a surface process, involving in Pt
 415 surface conducting and H⁺ ion diffusion and spillover along Pt on zeolite. This is particularly
 416 appealing to eletcro-oxidation process of methanol, where a more visible H⁺ evaluation/re-oxidation
 417 peak was captured by electrode 15Ptanxcr4. The CO oxidation/reduction current due to the
 418 disassociation of CH₃OH is generally lower than that predicted by HCOOH, attributed by higher
 419 energy density of methanol than that of formic acid. Nevertheless, the low theoretical open circuit
 420 potential of methanol can lead to poison Pt surface much easier than that presented in formic acid
 421 [38, 44].



429 Fig. 5. The steady-state cyclic voltammetry of electrochemical oxidation of HCOOH and CH₃OH on
 430 Pt/Y Zeolite catalysts in a mixture solution of 2.5 mol dm⁻³ sulphuric acid (H₂SO₄) and 1 mol dm⁻³ of
 431 HCOOH or CH₃OH, respectively. CV measurement was taken until a clear stable CV curve obtained.
 432 (a) HCOOH oxidation; (b) CH₃OH oxidation.

433

434 4. Pt distribution on Y zeolite

435 4.1. Estimation of Pt particle size and Pt distribution

436 The Pt particle size and its geometry were estimated by using the mean value of the first nearest
 437 neighbouring coordination number of Pt atoms as a function of Pt cluster edge length [34].

438 The ex-situ EXAFS measurement data was adopted to estimate the Pt particle, as seen in tables 2
 439 and 3. This is mainly attributed by the following reasons: (1) the low goodness fitting value
 440 determined by the ex-situ data fitting, compared to those using in-situ EXAFS data; (2) Pt particles
 441 were fully reduced on zeolite in H₂ gas, along with well-preserved zeolite structure (i.e. BET surface
 442 area at 539 m²g⁻¹ or for 563 m²g⁻¹ for 15anxcr4 or 5anxcr4, respectively); and (3) Pt particles might
 443 not follow icosahedral model under a potential deposition for in-situ measurement. The diameter of
 444 average Pt particle size is likely to increase in an acidic solution [46], particularly under potential
 445 deposition in hydride region. Table 4 illustrates the number of Pt atoms and their distributions in a
 446 Pt cluster. The Pt particle size is estimated around 1.0 - 1.1 nm in diameter with 147 atoms in a Pt
 447 cluster for sample 15Ptanxr4 without excess H⁺ ions on zeolite and 5 wt% Pt loading samples (i.e.
 448 5Ptanxcr4 and 5Ptanxr4). However, a significant decrease of Pt particle size down to about 0.55 -
 449 0.82 nm is determined for sample 15Ptanxcr4 in the presence of excess H⁺ ions in zeolite structure,
 450 consisting of merely 13 to 55 atoms in a Pt cluster. The presence of H⁺ ions on zeolite surface may
 451 facilitate the change of the charge density of zeolite support oxygen, resulting in a large reduction of
 452 Pt particle size.

453

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457

458 Table 4 The average first nearest neighbouring coordination number of Pt atoms and the number of
 459 Pt atoms in a Pt cluster.
 460

Acronym name	15Ptancr4	15Ptanxcr4	5Ptancr4	5Ptanxcr4 ^a
\overline{N}_T from refinement - Pt	6.33	6.00	7.47	6.02
Total atom in a Pt cluster	147	13, 55	147	147
Particle size (nm)	1.0 - 1.1	0.55 - 0.82	1.0 - 1.1	1.0 - 1.1

461
 462 ^aOxygen neighbours present in the first Pt–O coordination shell.
 463

464 4.2. Pt active surface area and distribution on zeolite

465 The actual Pt loading was calculated using an edge jump from EXAFS subtraction [29].
 466 The surface area of Pt particle was determined via hydrogen adsorption and desorption peaks
 467 captured by cyclic voltammetry measurement in H₂SO₄ solution. Table 5 illustrates a comparison of
 468 Pt distributions on zeolite for 1.5 wt% and 5 wt% Pt loading samples.

469 A significant high Pt surface area was determined for sample 15Ptanxcr4. The actual Pt loadings on
 470 zeolite for samples 15Ptanxcr4 and 15Ptancr4 are 0.77 wt% and 1.52 wt% respectively, in consistent
 471 to Pt active surface areas of 103.57 m²g⁻¹ and 51.59 m²g⁻¹. The Pt surface area is found generally low
 472 for the samples of 5Ptanxcr4 and 5Ptancr4, estimated at 32.61 m²g⁻¹ and 21.47 m²g⁻¹, with
 473 correspondent to Pt loadings of 4.71 wt% and 7.76 wt%, respectively. The prepared Pt loading on
 474 zeolite for samples 15Ptancr4 and 5Ptanxcr4 is found consistent with the measured values for 1.5
 475 wt% and 5 wt% Pt loading on Y zeolite, whilst either a significant low or a significant high value is
 476 determined for samples 15Ptanxcr4 and 5Ptancr4, respectively.

477 The net Pt atoms per cm² (N_T) predicted for samples 5Ptancr4, 5Ptanxcr4, 15Ptancr4 and 15Ptanxcr4
 478 were followed an order of $26.42 \times 10^{17} > 16.16 \times 10^{17} > 5.21 \times 10^{17} > 2.64 \times 10^{17}$ per cm², respectively.
 479 This tendency of net Pt atom distribution per cm² is well reflected by Pt loading on Y zeolite. The
 480 associated Pt surface atoms per cm² on zeolite (N_S) were determined to be 13.11×10^{16} (for sample
 481 5Ptancr4) $> 15.11 \times 10^{16}$ (for sample 5Ptanxcr4) $> 7.64 \times 10^{16}$ (for sample 15Ptancr4) $> 7.77 \times 10^{16}$
 482 (for sample 15Ptanxcr4), respectively. This has provided a high level of Pt surface atom dispersions
 483 (defined as $N_S/N_T \times 100\%$) of 29.44% for sample 15Ptanxcr4, compared with the values of 14.66%,
 484 9.35% and 4.93% for samples 15Ptancr4, 5Ptanxcr4 and 5Ptancr4, respectively. In general, the
 485 excess H⁺ ions incorporated with Pt/Y zeolite electrocatalyst will result in a better Pt surface atom
 486 dispersion, compared to samples with Pt loading at same level without excessive H⁺ ion presence.
 487 The increase of Pt loading on zeolite from 1.5 wt% to 5 wt% loading does not provide a higher Pt
 488 surface dispersion.

489 The present study has shown that H⁺ ions enable to achieve high Pt distribution on zeolite, owing to
 490 the change of Pt d bond energy state. The high Pt surface area can contribute to improve the Pt
 491 electrocatalytic activity using Nafion[®] bound Pt electrode, i.e. 15Ptanxcr4 or 5Ptanxcr4. This has
 492 been clearly reflected by the electrochemical reactions on Pt surface as (1) hydrogen

493 oxidation/reduction in hydride region in 2.5 mol dm^{-3} H_2SO_4 solutions, and (2) the oxidation of small
 494 organic species, i.e. HCOOH and CH_3OH species, in a 2.5 mol dm^{-3} H_2SO_4 electrolyte solution
 495 containing 1 mol dm^{-3} HCOOH or CH_3OH species. The increase of Pt loading on zeolite is able to
 496 facilitate the oxidation of HCOOH or CH_3OH species, which supports the evidence found by Kaur et
 497 al. [23].

498 For electrocatalysts, i.e. 15Ptanxcr4 and 5Ptanxcr4, H^+ ions act in a very similar way as other ions
 499 such as K^+ , Ca^{2+} and Fe^{2+} to promote a better Pt particle distribution by anchoring Pt on the zeolite
 500 surface and supercage wall to restrain Pt migration. Present CV measurement implies that the Pt
 501 particle sizes and their distributions on zeolite are indeed one of major contributors to determine
 502 the Pt oxidation and reduction performance.

503

504 Table 5 The comparison of Pt distributions on zeolite for 1.5 wt% and 5 wt% Pt loading samples.

Electrocatalyst	15Ptanxcr4	15Ptanxcr4	5Ptanxcr4	5Ptanxcr4 ^a
Pt active surface area m^2g^{-1}	51.29	103.57	21.47	32.61
Calculated mass quantity in wt %	1.52	0.77	7.76	4.71
N_T Pt net atoms per cm^2 ($\times 10^{17}$)	5.21	2.64	26.62	16.16
N_S Pt surface atoms per cm^2 ($\times 10^{16}$)	7.64	7.77	13.11	15.11
Dispersion N_S/N_T (%)	14.66	29.44	4.93	9.35

505

506 Note: N_T is Pt total atoms per cm^2 ; and N_S is obtained from Benfield theory.

507

508 5. Conclusion

509 This paper has presented the characteristics of zeolite supported Pt nano-particle and their
 510 electrocatalytic performances by EXAFS analysis and CV measurements. The resultant data analysis
 511 indicates that H^+ ions were able to restrain the mobility of Pt on zeolite during precursor thermal
 512 treatments by anchoring Pt on zeolite cage wall, leading to a high dispersion of Pt on zeolite and a
 513 better electrocatalytic performance, i.e. 15Ptanxcr4 and 5Ptanxcr4, compared to samples without
 514 the excess H^+ on zeolite, i.e. 15Ptanxcr4 and 5Ptanxcr4.

515 The Pt-Pt binding distance was measured between 2.75 \AA and 2.77 \AA , indicating the metallic nature
 516 of Pt. The 0.1 \AA or 0.2 \AA increase of Pt-Pt binding distance over a standard value of 2.75 \AA could be
 517 attributed by either electrochemical adsorption of H atom on Pt active surface forming a Pt-H bond
 518 or the interference of zeolite support oxygen as a result of increasing oxygen charge density. This
 519 can facilitate the oxidation of CH_3OH and HCOOH species, as evidenced by CV measurement using
 520 sample such as 5Ptanxcr4.

521 The hydrogen spillover pathway was explored by depicting the charger/electron transfer at Pt
 522 electrode and solution interface by either the direct charger transfer or the mobility of $\text{H}_{\text{ads}}/\text{H}^+$
 523 species on zeolite, which is a DC electrical insulator. The H^+ ions were found able to transmit along
 524 the zeolite surface to increase the surface conductivity of catalyst. The H^+ and H_3O^+ ions may also

525 lead to ionic conduction via free species by hitching a ride on water to increase the electrode surface
526 conductivity. In general, HCOOH has shown a better oxidation performance than that of CH₃OH.

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