Proton Modified Pt Zeolite Fuel Cell Electrocatalysts

Jun Yao[1*], Yufng Yao[2] and Hossein Mirzaii[3]

1-School of Engineering, University of Lincoln, Brayford Pool, Lincoln LN6 7TS, UK

jyao@lincoln.ac.uk

2-Faculty of Environment & Technology, School of Engineering Design and Mathematics,
University of West England, Frenchay Campus, Cold harbor Lane, Bristol, BS16 1QY, UK

yufeng.yao@uwe.ac.uk

3-Faculty of Science, Engineering and Computing, Kingston University, Roehamton Vale,
Friars Avenue, London SW15 3DW, UK

H.Mirzaii@kingston.ac.uk

Abstract

NaY Zeolite is selected as a suitable material to host 1.5 wt% Platinum (Pt) loading on zeolite using ion exchange method (a) $Pt(NH_3)_4(NO_3)_2$ without excess NH_4NO_3 nitrate and (b) $Pt(NH_3)_4(NO_3)_2$ with excess NH_4NO_3 nitrate. The structure/reactivity relationship of Pt nanoparticle has been experimentally studied via Nafion$^@$ bound electrodes to investigate the interaction nature of Pt with zeolite and electron transfer using the extended X-ray adsorption fine structure (EXAFS) and Pt particle was predicted at 0.7 – 1.5 (nm). Pt oxides can be electrochemically reduced via a hydrogen ‘spillover’ phenomenon. A highly dispersed small Pt particle distribution can be achieved with excessive H^+ ions on zeolite acidic sites.

Keywords: Pt/Y zeolite electrocatalyst, Nanoparticle, CV, EXAFS, Fuel cell

1. Introduction

Pt is a practically important catalyst of polymer electrolyte membrane fuel cell (PEMFC), because of its specifically high catalytic properties to promote the high energy density. Unfortunately, Pt is an extremely expensive metal which performance degrades very fast to hinder the fuel cell wide application. Hence, the creation of higher Pt active surface with less metal content is an utmost important goal in fuel cell related electro-catalyst research today.

The carbon nanotube or zeolite to facilitate the adsorption of small catalyst particles are reported as a solution for the particle cluster size control problem [1]. The excessive hydrogen ion exchanged zeolite has rich proton on zeolite acidic centers to form hydroxyl groups with oxygen, leading to the interaction of the metal precursors with zeolite and decrease the sintering propensity of metal [2]. Nevertheless, the surface oxygen groups, which form the anchoring sites for metallic precursors and metals, are well known to determine the catalyst supporting material properties [3]. Koningsberger et al [4] has investigated the influence of oxygen atom charge transfer on zeolite using the extended X-Ray adsorption Fine Structure (EXAFS). The increasing of electronegativity nearby the support oxygen atoms was found to increase zeolite alkalinity. The interaction between Pt and oxygen moves Pt electrons nearer to oxygen. A charge transfer can subsequently occur from or to Pt metal particles. This has particularly accounted for the PtHY zeolite catalyst, as H^+ ions exchanged into zeolite structure might result in an increase in the O, Si and Al binding energy.

A highly dispersed Pt/zeolite catalyst using O_2 calcination and H_2 reduction process is reported by Sachtler and Gallezot [5]. Pt is found favourable to locate in supercages at 300 ^oC with particle size of 6 – 13 Å. The XPS study has detected Pt particle migration through zeolite supercages to sodalite cages at calcination temperature of 450 ^oC [6]. Pt constrained within zeolite supercages are varied from single atom to particle in the order of 1 – 2 nm [7], forming a cluster of 10 to 25 atoms [8]. Pt-Pt binding energy is found to increase with Pt electron deficiency. An average of approximately 20 to 30 atoms with 11.3 Å per particle was predicted at the reduction temperature of 300 ^oC and was increased to 16 Å at 500 ^oC in H_2 [9]. Yokoyama et al. [10] also revealed that the Pt-Pt bonding distance of Pt cluster encaged in zeolite supercages was shorter than the bulk Pt metal. This suggested that the charge transfer from Pt clusters to the substrate was strong in the Pt/Y zeolite catalyst. The contraction of Pt-Pt bond distance on zeolite was due to the increase of Pt-Pt bonding energy caused by electron deficiency.

Zeolite is a well known dc insulator [11]. However, zeolite capability of solution – like ionic conduction [11] linkage in common with electrochemical environment indicates that the electrochemical reaction on Al-Si zeolite is able to occur in a charge – balanced ionic environment [12]. Pt metal particles are able to be completely hydrated and dehydrated due to a great capacity for water on zeolite [12]. The role of high water content in electrochemical reaction is considered to facilitate the spillover of hydrogen [13]. The water can act as vehicle to transport ions through zeolite free volume space by hitching a ride on water. This phenomenon is called spillover [14], mainly involving hydrogen and oxygen – containing species and is observed on catalyst such as Pt/C [15], Pt/SiO_2 [16], Pt/Al_2O_3 [17] and Pt/zeolite [18] in gas phase. Therefore, it is necessary to investigate H^+ spillover effect in zeolite – supported Pt│ Nafion@ bound Pt zeolite electrode system [7].

This study contributes to the understanding of electron transfer at the interface of Pt/zeolite electrode and solution and Pt particle size associated electro-catalytic efficiency in electrochemical reaction. The structure of the Pt particle was investigated using the extended X-Ray Adsorption Fine Structure (EXAFS) with correspondent Pt electrocatalytic performance was determined via cyclic voltammetry (CV) measurement.

2. Experimental

The 1.5 wt% Pt loading was made by ion exchange of Pt^{2+} ions with Na^+ on Y zeolite using either $Pt(NH_3)_4(NO_3)_2$ or $Pt(NH_3)_4(NO_3)_2/NH_4NO_3$ solution. The ion exchange procedure was followed by methods developed by Boyan [8] and Lalchan [19] at natural condition. The Pt microstructure synthesis was then followed the procedure developed by Gallezot and co-workers [6]. The samples were calcined at 350 °C in O_2 and were reduced in H_2 at 400 °C.

The Nafion@ bound electrode was made by spreading a thin paste of 1.5 wt% Pt/Y zeolite or Pt/HY zeolite and carbon powder (untreated XC-72R carbon powder) mixture with Nafion@ solution (5 wt% solution in lower alcohols from Aldrich) to carbon paper (E-TEK TGHP-90). A disc of 2.5 cm^2 diameter of electrode was cut for cyclic voltammetry measurement and 1.3 cm^2 diameter for EXAFS study via Hg/Hg_2SO_4 Mercury/Mercurous Sulfate (MMS) reference electrode. The electrolyte was 2.5 and 1 mol cm^{-3} sulphuric acid (H_2SO_4) solutions for Laboratory cyclic voltammetry and in-situ EXAFS measurements respectively using a computer-controlled potentiostat (Auto-Lab PGSTAT20) at a constant scan rate (dE/dt) of 1 mV/s [20]. The oxidation/reduction of the electro-active species of interest was detected between -0.65 V and 0.5 V, in which no any decomposition occurs [21]. The Extended X-ray Absorption Fine Structure (EXAFS) measurements were performed using the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, UK. The wiggler beam line was operated at 2 GeV and 100 mA. The high-order harmonics were removed using a double-crystal Si220 monochromator. The Pt L_{III} absorption edge was located by 50% detuning of a harmonic beam with a Pt foil used as a reference sample for EXAFS data collection.

3. Results and Discussion

3.1 Zeolite BET surface areas measurement

Zeolite crystalline structure was characterised by Brunauer-Emmett-Teller (BET) surface area measurement. Figure 1 depicts the zeolite BET surface area measurement for electrocatalysts such as 1.5 wt% Pt loading on zeolite calcined at 350 °C and reduced at 400 °C (i.e. 15PtANCR4) and 1.5 wt% Pt loading on zeolite made with excess NH_4NO_4 ion exchange calcined at 350 °C and 400 °C (i.e. 15PtANXCR4), respectively. The plain zeolite and carbon XC-72R powders are used as references which surface area was measured at $632m^2g^{-1}$ and $200m^2g^{-1}$ (table 1). The discrepancy of sample 15PtANXCR4 zeolite surface area is small, compared to plain zeolite. A well preserved zeolite crystalline structure was determined for sample 15PtANXCR4 made by excess NH_4NO_4 ion exchange method. The Pt zeolite electrocatalyst with no excess NH_4NO_4 ion change (i.e.15Ptancr4) has shown a significant reduction of zeolite surface area which was measured at $168m^2g^{-1}$, indicating the blockage of zeolite opening pores in small channel.

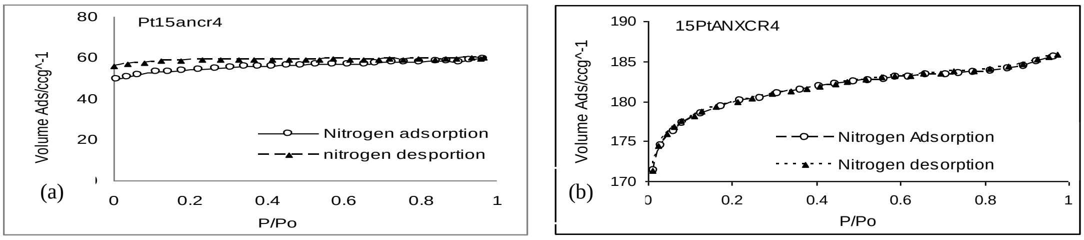


Figure1. Volumetric uptake of nitrogen at 77 K with absorption in open dotted line, and desorption in filled dotted line. (c) Sample15PtANCR4; (d) Sample 15PtANXCR4.

Table 1. BET surface area measurement for plain zeolite, untreated carbon XC-72R, 1.5 wt% Pt/Yzeolite(i.e.15PtANCR4) and 1.5 wt% Pt/HY zeolite (i.e.15PtANXCR4) electrocatalysts.

Acronym Name	Plain Zeolite Catalyst	Carbon XC-72R	15PtANCR4	15PtANXCR4
Surface Area m^2/g	623.2 ± 0.1%	200 ± 0.1%	168 ± 0.1%	539 ± 1.0%

3.2 The cyclic voltammetry (CV) measurement

The cyclic voltammetry (CV) measurement was performed in an electrochemical cell to determine the electro-activity of species using Nafion$^@$ bound electrode made by the mixture of Pt/zeolite electrocatalyst and carbon powder. The response of electrochemical reaction was determined by monitoring current change via potential. The CV measurement of 1.5 wt% Pt loading on Pt/Y zeolite carbon │ Nafion$^@$ electrodes (i.e. 15PtANCR4 and 15PtANXCR4) and 1.5 wt% Pt/C │ Nafion$^@$ electrode (i.e. 15Pt/XC-72R) made from a commercial available 40wt% Pt/XC-72R carbon catalyst mixed with the extra XC-72R carbon is depicted in Figure 2 to investigate hydrogen adsorption/desorption activity on Pt at -0.65 V in 2.5 mol dm^{-3} H_2SO_4 solution. Figure 2a depicts the CV of 1.5 wt% Pt/CX-72R electrode consisting of three distinguished regions, a hydrogen adsorption/desorption region (peak A) starting at potential region of -0.32 V to -0.65 V; oxide region; and the double layer region. The peak B is responsible for a hydrogen evolution and the peak C is linked with the weakly adsorbed H^+ ions forming covalent bond on Pt. The H re-oxidation (peak D) is observed on the hydrogen re-oxidation (HRO) region of -0.65 V to -0.36 V and the peak E is associated to weakly bound H desorption. The increase of current between 0.12 V and 0.5 V indicates the formation of Pt oxide species correspondent to an oxide stripping region of 0.5 V to 0.02 V. A charge separation is determined in a double layer region from 0.02 V to -0.36 V and -0.36 V to 0.12 V in a reverse sweep manner. Figure 2b has shown a consistent electrochemical oxidation/reduction features for sample 15PtANCR4 and 15PtANXCR4. A strong hydrogen adsorption peak has been observed at -0.6V and -0.56V for electrodes 15PtANCR4 and 15PtANXCR4. No weakly bound hydrogen adsorption peak was determined, as both weakly and strongly bound hydrogen may adsorb similar amount of energy, resulting in difficulty to distinguish them unless a much slow sweep rate less than 1 mV/s used. A hydrogen desorption peak was detected at -0.56V, followed by hydrogen evolution at -0.65V. The large hydrogen coverage is observed for 15PtANXCR4. The electrochemical responses coincide to that has been evident by Konigsberg and his co-workers [22]. The excess NH_4NO_3 on zeolite can result in small and well dispersed Pt clusters inside zeolite cage.

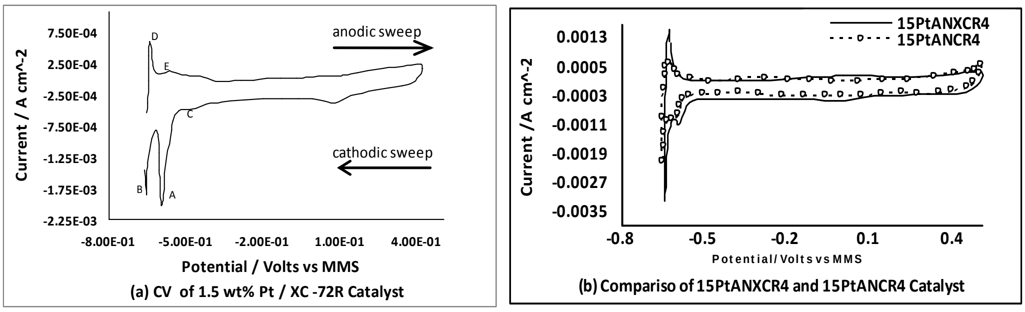


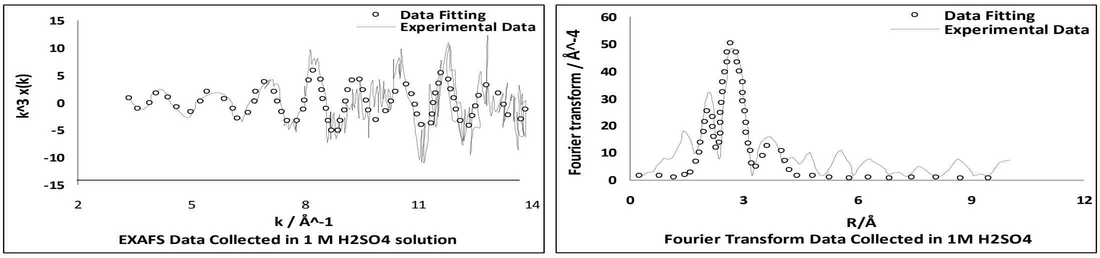
Figure 2. The steady state CV curves are measured at a scan rate of 1 mV/s in 2.5 mol dm^{-3} H_2SO_4 solution. (a) Sample 15Pt/XC-72R, (b) the comparison of CV for samples 15PtANCR4 and 15PtANXCR4.

The presence of electron/ion transfer at interface of Nafion$^@$ bound Pt/zeolite electrode and electrolyte solution has been demonstrated via CV. Gallezot et al [22, 23] predicted Pt particles more likely remained in zeolite supercage at reduction temperature of 400 ^{o}C, where electrochemical species were easy to access on zeolite Pt active site. Zeolite is a type of dc electronic insulator material that can't be used as direct electrode materials. However, zeolite is capable of solution – like ionic conduction which can act as an electron bank to contribute electrons to or garner electron from a reactant [24]. This links in common with electrochemical environment for reaction to occur in a charge – balanced ionic environment.

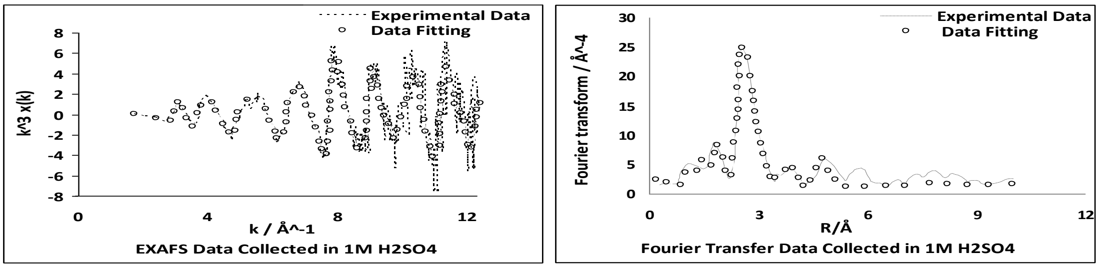
Hydrogen 'spillover' pathway on Pt/C catalyst was investigated by Srinivas and Rao [25]. The hydrogen adsorption/desorption can occur on carbon based Pt active sites. Later study by McBreen [26] has revealed the current generation on Pt active sites, remotely from conducting material surface with fast surface mobility of adsorbed species on the electrode. Therefore, the surface active sites of Pt particles not in direct contact with solid conductive polymer electrolytes might be also involved in an interfacial process through the pathway of surface conductance. The two possible pathways either the surface mobility of adsorbed species or hydrogen adatoms/H^+ ion may spill over through zeolite framework or on electrode surface [13] in which hydrogen ions (H^+) were able to form OH group with carbon/zeolite acidic surface oxides. Hydrogen spillover on Pt and zeolite acidic sites has been studied in gas phase [18], in which an anti – bonding state of Pt-H interaction relating to the electronic properties of the catalytic active sites has been observed [4]. This may be also adopted to implicate the hydrogen spillover between Pt electrode and solution in electrochemical environment. H^+ spillover may occur during the surface diffusion process of the absorbed species [18]. Water is an important spice to facilitate hydrogen migrating between zeolite and Pt. The electron transfer may take place between electrode and solution via free species, such as H^+ and H_3O^+. Ions are transported through free species by hitching a ride on water during their migration through zeolite channels and between the interface of electrode and solution.

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

Figure 3 illustrates the EXAFS data fitting for electrocatalysts 15PtANCR4 (with no excess nitrate ion exchange) and 15PtANXCR4 (with excess nitrate ion exchange). The correspondent fitting results are presented in Table 2. The in-situ EXAFS data was collected at Pt L_{III} edge at room temperature at -0.65 V in 1.0 mol dm^{-3} H_2SO_4 solution. The curve fitting (in dotted lines) matches the general form of the raw data (in dashed lines) very well and the data fitting was extended up to 3 shells with shell 1 and shell 2 predicted for Pt and shell 3 for oxygen, respectively, for electrocatalyst 15PtANCR4. The Pt coordination numbers in shell 1 and shell 2 were approximately 7.45 and 2.05. The introducing of third Pt-O shell has a significant improvement of data fitting quality. The first shell Pt cluster was predicted with Pt-Pt distance of 2.77 Å implicating the preserving of the bulk Pt characteristics. The Pt-O bond may attribute to the direct link of Pt associated with oxygen on zeolite Lewis acidic site .or the increase of Pt electron deficiency associated to either zeolite acidity or the decrease of Pt-Pt bonding energy, leading to a slight increase of Pt-Pt bond (2.77 Å), compared to the standard metallic Pt bond of 2.75 Å. The curve fitting for 15PtANXCR4 is extended up to 2 shells. Pt atom is fully reduced as no oxygen atom is predicted at neighbouring Pt shell. The total Pt atoms are fitted up to two shells at 7.86, indicating Pt particle size small for excess nitrate salt ion exchanged electrocatalyst 15PtANXCR4, compared to sample with no excessive H^+ presence (i.e. 15PtANCR4) with an average of 9.50 atoms. Pt particle size is estimated at 1.5 nm and 0.8 nm for samples 15PtANCR4 and 15PtANXCR4, respectively.



(a) 15PtANCR4



(b) 15PtANXCR4

Figure 3. The in-situ EXAFS data fitting for 1.5 wt% Pt Y zeolite catalysts with phase corrected. The experimental data and the fitting results are presented in dashed line and dotted line, respectively. Data is collected at -0.65 V vs MMS reference electrode in 1.0 mol dm^{-3} H_2SO_4 solution under potential deposition. The EXAFS data was collected at Pt L_{III} edge at room temperature. (a) Electrocatalyst 15PtANCR4, (b) Electrocatalyst 15PtANXCR4.

Table 2. The data fitting results for 1.5wt% Pt/Y Zeolite for electrocatalysts 15PtANCR4 and 15PtANXCR4 at -0.65 V in 1.0 mol dm^{-3} H_2SO_4 solution.

15PtANCR4	Atom coordination	Shell 1 - Pt	Shell 2 - Pt	Shell 3 - O
	N	7.45	2.05	0.75
	R (Å)	2.77	3.85	2.19
15PtANXCR4	N	6.38	1.48	no
	R (Å)	2.77	3.90	No
N = coordination number; R = coordination distance				

4. Pt active surface area measurement and Pt distribution on zeolite

Pt active surface area under hydrogen peak is measured at $103.57 m^2/g$ for 15PtANXCR4 and $51.29 m^2/g$ for 15PtANCR4, correspondent to 0.77 wt% and 1.52 wt% Pt loading on zeolite (table 3 & figure 4), respectively. The results are consistent to Pt surface atom distribution. The total Pt atoms per cm^2 correspondent to Pt loading for sample 15PtANXCR4 have a 50% reduction, compared to sample 15PtANCR4. Pt surface atom dispersion is 29.44% and 14.66% for catalysts 15PtANXCR4 and 15PtANCR4, respectively.

Table 3. Pt active surface area m^2 per gram

Sample	15PtANCR4	15PtANXCR4	15Pt/XC-72R	Dispersion N_S/N_T (%)
Pt active surface area under H Area/m^2/g	51.29	103.57	0.133	14.66
wt% Pt	1.52	0.77	1.49	29.44

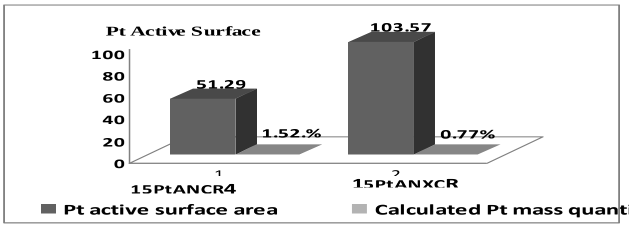
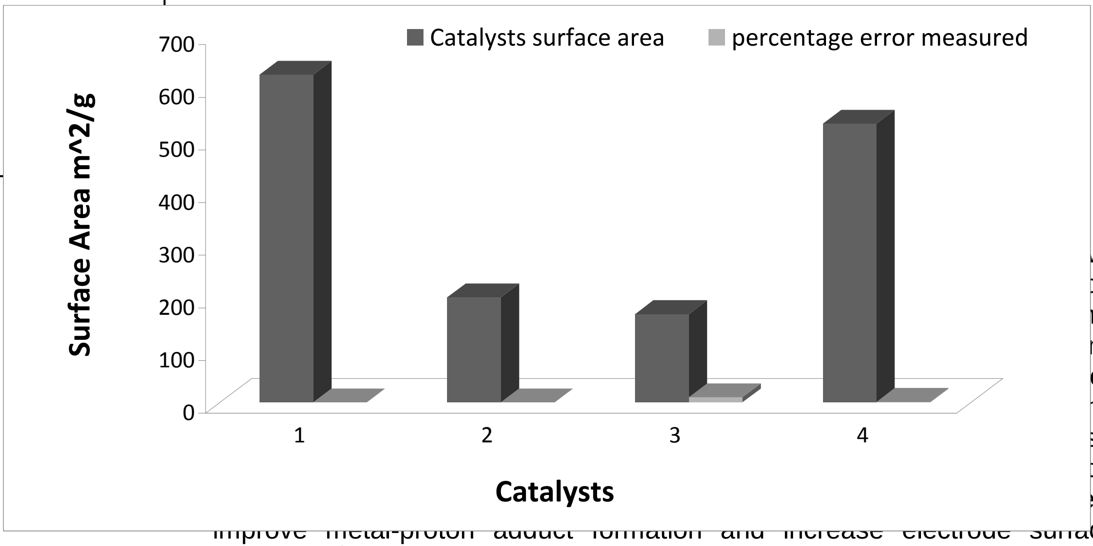


Figure 4. The comparison of Pt active surface area distribution on zeolite.

The present study has shown that a highly dispersed Pt particle distribution on zeolite can be achieved with the presence of excessive H^+ ions on zeolite. The zeolite acidity may affect Pt catalytic activity, as the formation of metal – proton adducts results in Pt electron change and hydrogen spillover phenomenon. The spillover H^+ ions can be transmitted along the surface of the zeolite support to increase the surface conductivity of the support [27].



ween zeolite and Pt
Pt particle size, Pt
ical control and the
mogram feature of
cess or no excess
nsistent to 1.5 wt%
surement indicates
15PtANCR4. The
sites. H^+ is able to
improve metal-proton adduct formation and increase electrode surface conductivity by spillover H^+ on zeolite. Water is important for hydrogen migration via free species, such as, H^+ and H_3O^+, by hitching a ride on water. Pt particle cluster is predicted at 0.8 nm for catalyst 15PtANXCR4 and 1.5 nm for catalyst 15PtANXCR4, correspondent to Pt distribution of 29.44% and 14.66% with Pt loading of 0.77 wt% and 1.54 wt%, respectively. Conclusively, 1.5 wt% Pt loading on zeolite made by excess nitrate (i.e. 15PtANXCR4) has shown a great advantage to provide high surface area with efficient mass transport capacity for electroactive species to and from electrode surface in comparison of those without excess nitrate ion exchanged electrcatalysts (i.e.15PtANCR4).

6. Reference

1. H.N.Yang, J.Y.Lee, Y.Na, S.C.Yi, W.J.Kim, Microporous and Mesoporous Materials 152 (2012) 148-156.
2. F. Rodriguez-Reinoso, The role of carbon materials in heterogeneous catalysis, 1998; 36:159-75.
3. E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl Catal A, 1998;173:259-71.
4. D.C. Koningsberger, J de Graaf, B.L. Mojet, D.E. Ramaker, J.T. Miller, Applied Catalysis A: 191 (2000) 205 -220.
5. W.M.H. Sachtler and Z. Zhang, Advances in Catalysis, 1993, 39: p.129.
6. P. Gallezot, A. Alarcon-Diaz, J.A. Dalmon, A.J. Renouprez, B. Imeuk, J. of Catalysis, 1975, 39: p.334.
7. D.R. Rolison, E.A. Heys, W.E. Rudzinski, J. of Physical Chemistry, 1989, 93: p.5524.
8. B.I. Boyanov and T.I. Morriso, J. of Physical Chemistry, 100 (1996) 16310-16317.
9. K.I. Pandya, S.M. Heald, J.A. Hriljac, L.Petrakis, J. Fraissard, J. of Physical Chemistry, 1996, 100: p.5070.
10. T. Yakoyama, N., Kosugi K. Asakura, Y. Iwasawa and H. Kuroda, Journal De Physique Colloques, 47 (1986) C8-273.
11. D.W. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Use, 1974, Wiley-Interscience, New York, p.397.
12. D.R. Rolison, J. of Chemical Review, 1990, 90: p.867.
13. W.J. Liu, B. L. Wu, C.S. Cha, J. of Electroanalytical Chemistry, 476 (1999) 101 -108.
14. P.A. Sermon, G.C. Bond, Catal. Rev. 8 (1973) 211.
15. V.S. Bagotzky, L.S. Kanevsky, V.S. Palanker, Electrochim. Acta 18 (1973) 473.
16. J.F.C. Candau, W.C. Conner, J. Catal. 106 (1987) 378.
17. R.R. Cavanagh, J.T. Yates Jr., J. Catal. 68 (1981) 22.
18. A. Zhang, Ikusei Nakamura, Kaoru Fujimoto, J. of Catalysis, 168(2) (1997) 328-333.
19. P. Lalcha, A.J. Bard, A. Campion, M.A. Fox, T.E. Mallouk, S.E. Webber, J.M. White, Inorg. Chem., 1987, 28: p.3825.
20. Heinz Geaischer and Charlesw Tobias, Advances in Electrochemsitry and Electrochemical Engineering, Vol 11, 1978.
21. Christopher M.A. Brett and Ana Maria Oliveira Brett, Electroanalysis, 1998, Oxford University Press.
22. Z. Zhnag, T.T. Wong, W.M.H. Sachtler, J. of Catalysis, 1991, 128: p13.
23. P. Gallezot, Catal. Rev. Sci. Eng., 1979, 20: p121.
24. G. Larsen, G.L. Haller, Catalysis Letters, 1989, 3: p103.
25. S. Srinivas, P. Rao, J. Catal. 148 (1994) 470.
26. J. McBreen, J. Electrochem. Soc. 132 (1985) 1112.
27. J.M. Herrmann, J. Catalysis, 1984, 89: p404.