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

Jun Yao [a,*], Yufeng Yao [b]

[a] School of Engineering, University of Lincoln, Brayford Pool, Lincoln, LN6 7TS, UK
[b] Department of Engineering Design and Mathematics, University of the West of England, Bristol, BS16 1QY, UK

ARTICLE INFO

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 CH_3OH 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.

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

Zeolite can provide an environment to produce highly dispersed Pt metal particle, owing to its high selectivity and great capacity of absorbing and retaining water by the creation of zeolite proton conducting membranes for solution like ionic conduction through interconnecting channels without damaging the zeolite crystalline lattice structure [2–4]. The growth of Pt particle on zeolite is mainly controlled by O_2 calcination step in gas phase and high dispersion of Pt can be achieved by further H_2 reduction step [5]. A slow heating process at a high O_2 flowrate would be preferable to avoid Pt

non-uniform distribution on zeolite introduced by auto-reduction [6] that may produce large Pt metal particles during the removal of ammonia ligands at 300 °C [7–9]. Pt is also found favourable to remain in the zeolite supercage at 350 °C in O_2 and 400 °C in H_2, respectively, resulting in a particle size of 0.6–1.3 nm, which is much smaller than that of graphene based materials with Pt particle size growing up to 1.5–19 nm [10].

Pt was more stable at zeolite sodalite cage, mainly due to its strong polarization nature of the Pt-d bond electron configuration [11]. A high degree of Pt dispersion was reported in the presence of H^+ ions by forming Pt–H adduct in zeolite structure. H^+ ions can act as a chemical anchor to diminish the sintering of Pt particles at 400 °C in H_2. The polarization of Pt particles by the nearby cations, i.e. H^+, might result in the electron deficiency of Pt, leading to the change of Pt catalytic activity and spectroscopic properties [12,13]. Moreover, the charge transfer between Pt and nearby neighbouring zeolite support oxygen atoms can play an important role during this process [14,15].

The disorder of Pt particle on zeolite framework has had a dramatic effect on the Pt electronic structure by the extended X-ray adsorption fine structure (EXAFS) [16,17]. The Pt–Pt bond distance was shortened to less than 2.75 Å than that of Pt bulk metal in the presence of strong charger transfer between Pt clusters with the increase of the Pt–Pt binding energy due to Pt electron deficiency [18], compared to Pt in a non-zeolite supported system, i.e. Pt/SiO_2. Vaarkamp et al. [19] predicted an average Pt particle size consisting of approximately 15 atoms with the first shell coordination number and Pt–Pt distance of 5.5 and 2.75 Å, respectively.

The electrochemical activity of Pt nanostructure on zeolite was previously investigated by Rolison [4]. The Pt was found to exhibit particular chemical and physical characteristics that could enhance the electrochemical reaction, owing to high ionic strength between electrodes. Liu et al. [20] suggested that hydrogen spillover is an important process to promote Pt electrocatalysis for Pt/C electrode. The H^+ ions adsorbed on the Pt active surface could spillover and diffuse into the surface of the inert support to form acidic surface oxides for an interfacial reaction of electrocatalytic process being taken place on Pt surface. The spillover of hydrogen has been discovered in both Pt/Al_2O_3 and Pt/SiO_2 catalyst systems to promote the transport of an active species between catalyst active sites. Zhang et al. [21] also observed hydrogen spillover from Pt to zeolite Brønsted and Lewis acidic sites in gas phase.

Pt appears to be one of the best catalysts for dissociating the C–H bound at a relatively low potential [22], which is favourable to oxidise small organic species, such as, methanol (CH_3OH) 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 CH_3OH 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 CH_3OH 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.

Experimental

Pt/Y zeolite electrocatalysts ion exchanged using $Pt(NH_3)_4(NO_3)_2$ or $Pt(NH_3)_4(NO_3)_2/NH_4NO_3$ salts

The 1.5 wt% and 5 wt% Pt loading on Y zeolite electrocatalysts was made by ion exchange method [17,18] using $Pt(NH_3)_4(NO_3)_2$ salt (denoted as 15Ptancr4 for 1.5 wt% Pt loading and 5Ptancr4 for 5 wt% Pt loading on Y zeolite thereafter) or $Pt(NH_3)_4(NO_3)_2/NH_4NO_3$ salt (denoted as 15Ptanxcr4 for 1.5 wt% Pt loading and 5Ptanxcr4 for 5 wt% Pt loading on Y zeolite thereafter) in neutral solution, respectively.

An appropriate quantity of $Pt(NH_3)_4(NO_3)_2$ was thoroughly dissolved in 200 ml of triply distilled water. The ion exchange process was then taken place in water-jacketed reactor, where the sodium Y zeolite powder was dispersed at a concentration of 1 g per 100 ml. The Pt ion was slowly added by pumping $Pt(NH_3)_4(NO_3)_2$ salt solution into the reactor. The sample was then washed with triply distilled water until no $[Pt(NH_3)_4]^{2+}$ complex detected by Ultraviolet (UV) [27]. After washing, sample was later dried overnight in an oven.

In case of the excess nitrate ion exchange method using $Pt(NH_3)_4(NO_3)_2/NH_4NO_3$, the NH_4NO_3 was added firstly into the suspended zeolite using stoichiometric titration method to provide a NH_4NO_3 concentration of 0.063 mol dm^{-3} prior to the adding of the $Pt(NH_3)_4(NO_3)_2$ salt.

Calcination and reduction

The synthesis of Pt nanostructures on Y zeolite was carried out by applying the calcination and reduction procedure to remove the Pt co-ordinate ligand, i.e. a crucial chemical step