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Full Length Article

Effect of different zeolite as Pt supports for methanol oxidation reaction

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ABSTRACT

In this work, we investigate the effect of zeolite–carbon composite as support of Pt (Pt/zeolite-carbon) on the electrocatalytic activity for methanol oxidation reaction (MOR) in acid media. Three different zeolites were evaluated: faujasite (FAU), merlinoite (W) and analcime (ANA). Zeolite-carbon substrate and Pt nanoparticles were synthesized by sol gel and ultrasound, methods, respectively. FAU zeolite exhibits higher specific surface area constituted by micro and mesoporosity compared to ANA and W zeolites, which are characterized by their mesoporous structure. TEM results shows that Pt/FAU-C enhances the formation of smaller Pt clusters compared to Pt/W-C and Pt/ANA-C which exhibit a homogeneous Pt dispersion. XRD results indicate that Pt/zeolite-C shows different intensity of Pt crystallinity. XPS analysis indicated the presence of Pt^0 and Pt^{2+} on the electrocatalysts. The content of Pt^0 was influenced by the nature of the support evaluated. The Pt/FAU-C electrocatalyst exhibited higher electrochemical activity for MOR showing the lowest onset potentials and the highest oxidation current of methanol compared to Pt/W-C, Pt/ANA-C and Pt/C. It was associated with the intrinsic properties of substrates that modify the size, dispersion, crystallinity, electronic density and hydrogen ion spillover for MOR.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFCs), which use hydrogen and methanol as fuel, respectively, have emerged as promising renewable power devices [1]. Methanol (CH_3OH) and ethanol (C_2H_5OH) used for the anode are considered an effective alternative fuel for electrochemical conversion, these alcohols are characterized by their advantages to be used as liquid fuel and theoretically higher energy density. The methanol electro-oxidation reaction (MOR) on Pt electrodes in acid solution takes place through the formation of physically adsorbed intermediates such as carbon monoxide (CO_{ads}) or formaldehyde ($HCHO_{ads}$) depending on the path followed. For ethanol oxidation reaction (EOR), acetaldehyde (CH_3CHO_{ads}) is formed as intermediate [2]. In the cathode, the oxygen reduction reaction takes place by following different mechanisms depending on the aqueous electrolytes. The Damjanovic model describes the oxygen reduction reaction (ORR) as a multi-electron reaction; the oxygen is directly reduced to H_2O through four-electron transfer, and to H_2O_2 via two-electron transfer [3–5]. Pt-based materials have been employed efficiently as catalysts of the two electrochemical reactions (oxidation and reduction) for direct alcohol fuel cells (DAFCs). However, Pt/C has drawbacks such as high cost and vulnerability toward poisoning by CO or carbonaceous intermediates [6,7]. In this way one of the major efforts in alcohol fuel cell catalysts research is to improve the electrocatalytic activity for alcohol oxidation and alcohol tolerance, as well as reducing its cost.

The incorporation of zeolites (crystalline aluminosilicates) in electrocatalyst for fuel cells has attracted the attention due to their properties. The stability of zeolites in acidic or alkali media allows them to act as second catalyst or support [8]. The former accelerates the ethanol oxidation reaction. As support the zeolites have protonic entities on their surface which make them more hydrophilic than carbon [2]. Additionally, the zeolite structure is characterized by possess Brønsted or Lewis acidic sites on zeolite framework that facilities the flow of protons through zeolite channels [9]. The presence of zeolite improves the long-term cycle stability of platinum catalyst during the ethanol electro-oxidation process [8]. Additionally, the zeolites facilitate the cleansing of catalyst surface by minimizing the formation of intermediates as CO_{ads}. The properties as molecular sieving promote the contact between the reactants and the catalytic active sites, enhancing the catalytic efficiency [2].

The synthesis process and modification treatment previous to obtaining of zeolite –modified electrode influence the redox performance. Consequently the type of zeolite has an important effect on the electrochemical activity of electrocatalyst.

One of the most reported zeolite is the Y zeolite that exhibits the

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faujasite topology. Particularly, faujasite (X, Y, and USY) presents a tridimensional channel system [10,11]. The Y zeolite has been studied in its acidic form, earth rare elements-zeolite (Ru, Pd, Pt, Ni) and as composite with carbon. Most of the reports evaluated the composite where the carbon or graphite is the main constituent, and the zeolite is the minor one. Ojani et al. [12] reported the electrochemical behavior of NiY-modified carbon paste electrode for methanol oxidation, where they found that the composite shows high stability toward methanol oxidation. Ouf et al. [13] evaluated an Au-Y zeolite /graphite electrode, they reported a high catalytic activity for ethanol oxidation in basic medium. Yao et al. [14] reported the Pt-Y zeolite as electrocatalyst for methanol and formic acid oxidation. They found that the electrocatalyst was better for formic acid. The X zeolite modified with Pt and Pt/Ru was evaluated as an electrocatalyst for carbon monoxide oxidation [15] and the Ni-X zeolite for methanol electrooxidation [16]. For these reasons in the present work we evaluated three zeolites: FAU (NaX), ANA (analcime) and Lynde type W. NaX zeolites possess a large void volume of 50% in their frame structure. This material is characterized by a cage comprising SiO_4 and AlO_4 tetrahedral bound by bridged oxygen atoms to make a 12-ring pore opening and tridimensional channel system. Due to these properties, the NaX zeolite is used as adsorbent, catalyst, and ionic exchanger [17,18].

Analcime zeolite is one of the most compositionally flexible framework structures [19]. It has a complex aluminosilicate framework, made up of linked tetrahedral units proscribing three non-connected channels and its small pores are arranged in four, six and eightfold rings [20,21]. The small pores of analcime make it important for technical innovations in selective adsorption and heterogeneous catalysis [22].

Lynde W zeolite is an analogue of the merlinoite-type zeolite, which is characterized by a tetragonal framework constituted by composite building units: double crankshaft chain, double eight member ring, and paulingite cage. The merlinoite topology comprises an interconnected set of eight member ring channels of different dimensions and directed along each of the three principal crystallographic directions [23].

For analcime and Lynde W zeolites few reports exist about their use as electrocatalyst supports for alcohol oxidation. Azizi et al. [24] reported the use of Ni-loaded analcime for electrooxidation of methanol; they prepared a modified electrode with carbon and Ni-analcime. They found that the electrocatalyst increases the kinetics of methanol oxidation and decreases the overpotential of the reaction in alkali medium.

Therefore the aim of this work was to evaluate the electrochemical activity of electrocatalyst zeolite based. The three zeolites FAU, ANA and W were synthesized from fly ash, considering that the content of carbon in the zeolite precursor enhances the electrical conductivity of the zeolite material. The pristine zeolite was submitted to two different methods in order to obtain the acidic form of the zeolites (zeolite-H) and the composites zeolite-C by addition of a 5% of carbon respect to silica content of each zeolite. Pt was incorporated to the supports by reduction method. The electrochemical activity for methanol oxidation reaction was investigated by using cyclic voltammetry (CV) and chronoamperometry (CA) techniques.

2. Experimental section

For the electrocatalysts synthesis three steps were performed: first one, synthesis of zeolites, second one preparation of the supports (zeolite-carbon composites and acidic form-zeolite) and third one the Pt nanoparticles preparation.

2.1. Materials

Hexacloraplatinic acid ($H_2PtCl_6{\cdot}6H_2O$), 5 wt.% solution of Nafion perfluorinated, isopropyl alcohol, methanol, and sulfuric acid were purchased from Sigma Aldrich. Fly ash was used as precursor for zeolite synthesis, the details and its properties are reported in Medina et al. [25]. Sodium and potassium hydroxides (Riedel de Haën) were used as mineralizing agents, aluminum hydroxide (J.T. Baker) was used for synthesis of composite zeolite –carbon. Ammonium chloride (Spectrum Chemical^{MFG}) was used for the preparation of the acidic form of the zeolites. All the reagents were of analytical grade. Distilled water was used as solvent.

Table 1
Physicochemical properties of the pristine zeolites.

Zeolite	Si/Al ratio	BET area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore size (nm)
FAU	1.59	299.15	0.330	4.40
ANA	2.06	40.35	0.118	11.75
W	2.09	28.48	0.132	18.5
FAU-C	–	102.60	0.123	5.50

2.2. Synthesis of zeolites

Three zeolites were synthesized: faujasite (X), Lynde W, and analcime. These zeolite materials were obtained by using fly ash, following the procedure reported in a previous work [25]. Briefly, W zeolite was synthesized by using 16 g of fly ash and KOH/fly ash ratio of 0.33 in aqueous medium. The suspension was subjected to a hydrothermal treatment at 175 °C for 16 h. For faujasite and analcime zeolites, sodium hydroxide was used as mineralizing agent; it was mixed with 7.6 g of fly ash at a NaOH/fly ash ratio of 0.83 and 1.04 for analcime and faujasite, respectively. The mixtures were subjected to heat treatment and then ageing. The crystallization conditions were 90 °C for 8 h for faujasite and 150 °C for 24 h for analcime. The zeolites were used to obtain different catalyst support: (a) acid form zeolite and (b) zeolite-carbon composite.

2.3. Preparation of the supports

(a) *Acidic form -zeolite*

In order to obtain the acidic form of the zeolites 30 g of the zeolite (FAU, W or ANA) were added to 100 mL of NH_4Cl 5 M solution and kept under stirring at 100 °C for 2 h. The solid was recovered, filtered and washed with deionized water. This procedure was repeated four times. At the end the exchanged zeolite was thoroughly washed with deionized water until it was made sure that the chloride ions were removed. Finally the solid was dried at 100 °C for 12 h. Afterwards the ammonia-zeolites were submitted to heat treatment at 300 °C for 2 h in air atmosphere. The samples were labeled as FAU-H, W-H and ANA-H.

(b) *Zeolite-carbon composite*

The obtaining of the zeolite-carbon composites was performed considering that the presence of zeolite enhances the durability and stability of the catalyst. Zeolites are characterized as an electrical insulator material, but it is capable of acting as ionic conductor in an electrolyte solution [26]. The incorporation of carbon powder could provide the electrical conductivity required for the transport of the electrons. For these reasons the composite supports were prepared through the incorporation of carbon Vulcan XC 72-R (5 wt.% respect to silica content) in the zeolites, bearing in mind that each zeolite possesses a different Si/Al ratio, the zeolite/carbon ratio was 2.5 for FAU zeolite, and 11 for W and ANA zeolites. The procedure was an adaptation of the sol gel method reported by Sandeep et al. [27]. Briefly, 125 mg of the zeolite was added to 10 mL of distilled water and kept under stirring. Then, carbon was added maintaining the stirring. Subsequently, the suspension was sonicated for 10 min. Afterwards, aluminum hydroxide (4 wt.% respect to the carbon content) was added. The slurry was kept under stirring for 24 h. Then it was washed with distilled water and dried at 80 °C for 24 h. The product was subjected to