

Methanol Electrochemical Oxidation on Modified Alumina Supporting Pt-single Atom Catalyst

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A facile procedure to synthesize Pt single atoms dispersed on Al₂O₃ nanoparticles, for methanol oxidation reaction (MOR), was proposed. An effective surface modification, to enhance overall electrocatalytic performance, was performed. Transmission Electron Microscopy (TEM), thermogravimetric analysis (TG), Fourier Transform Infrared Spectroscopy (FTIR), and X-ray diffraction (XRD) were employed for nanomaterial characterization. The catalyst showed a low onset potential of 0.04 V and a very high I_f/I_b ratio of 2.14. The results obtained in this work evidence the outstanding performances of the synthesized nano-electrocatalyst.

1. Introduction

In recent years, liquid alcohols have been regarded as a valid alternative to fossil fuels to be used either in direct alcohol fuel cells (DAFCs) or electrolyzers for the electrochemical production of hydrogen. Namely, methanol has received increasing attention by virtue of its higher energy density and ease of storage (Cloutier and Wilkinson, 2010). Methanol oxidation reaction (MOR), occurring at the anode of DAFCs, requires a catalyst capable of improving the sluggish reaction kinetic with the minimum energy supply. Pt-based materials have been employed efficiently as catalysts of the two electrochemical reactions (oxidation and reduction) for DAFCs. However, Pt/C use is hampered by two issues: high costs and vulnerability toward poisoning by CO or carbonaceous intermediates (Jeon and McGinn, 2010; Carrette et al., 2001). 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 reduce the costs.

Aluminum oxides (Al₂O₃) are a class of fascinating materials with widespread applications as adsorbents and catalysts (Passos et al., 2016; Samain et al., 2014). Particularly, γ -Al₂O₃ is one of the most employed supports for heterogeneous industrial catalysis. The assets of alumina include low cost, relatively high surface area, large porosity, and good chemical and thermal stability (Segal et al., 2018). Al₂O₃ also possesses special surface properties that certainly affect the ability of the catalytic systems (Robatjazi et al., 2019). Additionally, a simple NH₄BF₄ surface modification allows obtaining an improved amount of Brønsted acid sites on the catalyst framework that facilitates the flow of protons (Ueda et al., 2000) and the cleansing of the catalyst surface by minimizing the formation of intermediates as CO_{ads}. On the other hand, supported single-atom metals, maximizing atom efficiency, have been demonstrated as promising materials for C–H bond activation (Shan et al., 2017).

Herein, to develop enhanced and cheaper catalysts for MOR, Pt single atoms dispersed on alumina, modified by Brønsted acid sites, were prepared. Transmission Electron Microscopy (TEM), thermogravimetric analysis (TG-DTG), Fourier-transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) were employed for characterization. The electrochemical performances of the electrode were investigated by cyclic voltammetry and long-term chronoamperometry tests in CH₃OH solution. The results proved that this kind of electrode has remarkable electrochemical performance showing a low onset potential, a high I_f/I_b ratio, i.e. ratio between the peak current density in the forward scan and the peak in the backward scan, and improved electrochemical stability.

2. Experimental

2.1 Catalyst preparation

All chemicals were acquired from Sigma Aldrich and used as received without further treatment. The synthesis of γ - Al_2O_3 supported Pt was carried out by an impregnation method (Wang et al., 2020). Briefly, 300 mg of γ - Al_2O_3 was added into an aqueous solution (20 ml) containing platinum nitrate (Sigma Aldrich). The solution was stirred for 120 min, and, after, the water was removed by a vacuum rotary evaporator (Hei-VAP Core, Heidolph). Finally, the obtained material was dried at 105°C overnight and then calcined at 500°C for 180 min in air.

Pt/ Al_2O_3 catalyst modified with Brønsted acid sites was prepared by a sol-gel route. In particular, 150 mg of Pt/ Al_2O_3 was dispersed in 40 mL of distilled water (DW) and vigorously stirred, and 35 ml of NH_4BF_4 aqueous solution (1.85 mg/ml) was added in the suspension at 85°C. Nitric acid (1 M) solution was dropwise added in the suspension until to pH=3 (the pH solution was measured with a 3510 pH meter Jenway). The suspension was vigorously mixed for 2 h at 85°C. After, to reach pH 6, aqueous ammonia was dropwise added into the solution under stirring. The suspension was dried at 75°C for 24 h in air. The gel obtained was then washed with DW and dried at 85°C for 48 h. Finally, the sample was calcinated at 550°C for 4 h to obtain Pt/ Al_2O_3 @ NH_4BF_4 catalyst.

2.2 Characterization methods

Transmission electron microscopy (TEM) images were obtained by an FEI Tecnai electron microscope (200 kV). High-resolution analytical TEM (F20 FEI Tecnai-200 kV) was used for high-angle annular dark-field (HAADF) analysis. HAADF detector was employed in STEM mode. A Bruker D8 X-ray diffractometer with a monochromatic $\text{CuK}\alpha$ radiation was used for measurements of powder diffraction profiles. The thermal behavior of the samples was investigated using thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis (Mettler Toledo TGA, Model), between 25 and 1000 °C under air flow (60 mL/min) with a heating rate of 10 °C/min. FTIR was recorded on the Fourier transform infrared spectrometer BRUKER VERTEX-70, (Bruker Corporation), by applying KBr technique. Electrochemical tests of the synthesized samples, in particular cyclic voltammetry (CV) tests, were carried out by means of an Autolab PGSTAT302N potentiostat. For electrode preparation, 4 mg of catalyst were dispersed into 80 μl of a 5 wt% Nafion solution, 200 μl of ethanol and 800 μL of water (Sarno and Ponticorvo, 2020a, Sarno and Ponticorvo, 2020b). The subsequent mixture consists of a homogeneous suspension which, after being sonicated for 30 mins and then air-dried, was partially deposited dropwise onto a Screen Printed Electrode (SPE) (Rowley-Neale et al., 2015; Sarno et al., 2019a).

3. Results and Discussion

3.1 Catalyst characterization

Figure 1 shows TEM analysis of Pt/ Al_2O_3 . The image shows particles with a diameter of few nanometers. The aberration-corrected HAADF/STEM image of Pt/ Al_2O_3 is also shown in Figure 1. Contrast points, coherent with single platinum atoms, can be seen. EDX provided the Al, O and Pt maps, which are practically superimposable, supplying evidence of the homogenous distribution of the elements. Al/Pt atomic ratio, according to EDX evaluation, equal to 39.94/0.15, in good agreement with the amount of precursors used for synthesis, was found.

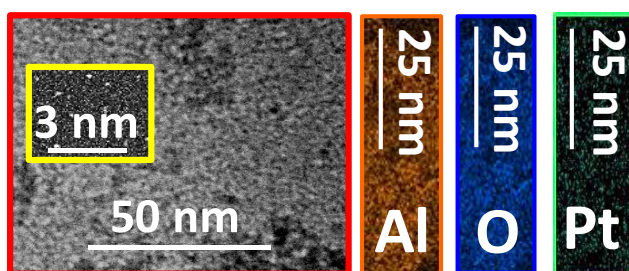


Figure 1: TEM image of Pt/ Al_2O_3 (red box), aberration-corrected HAADF/STEM image (yellow box), and EDX maps of Al, O, and Pt (orange, blue and green boxes, respectively).

The XRD pattern of Pt/ Al_2O_3 sample was shown in Figure 2. The X-ray diffraction pattern was acquired in the 2θ range of 20-90°. The result indicates some crystalline phases mixed with the primary amorphous structures of γ -alumina (Wang et al., 2016). No Pt peaks were detected from the XRD patterns, in agreement with the

single-atom nature of that Pt (Sarno et al., 2020). The TG-DTG analyses of the synthesized sample was carried out, and the results are displayed in Figure 3. The TG curve, with soft slopes and without sharp peaks, showed single phases and no impurity. Slight, but consecutive, weight losses were observed, which can be ascribed to samples' dehydration and the chemically adsorbed residual hydroxyl species decomposition (Gao et al., 2018).

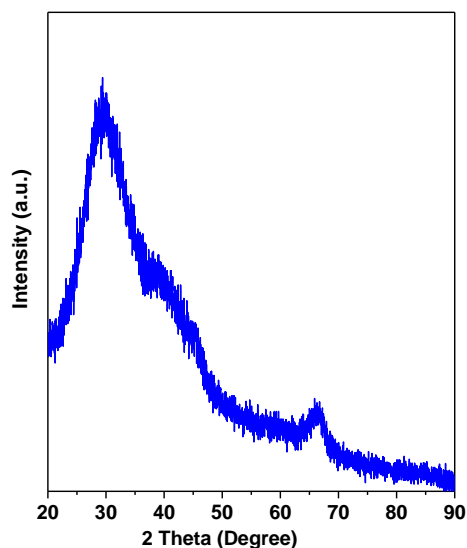


Figure 2: XRD spectrum of Pt/Al₂O₃ before the modification with NH₄BF₄.

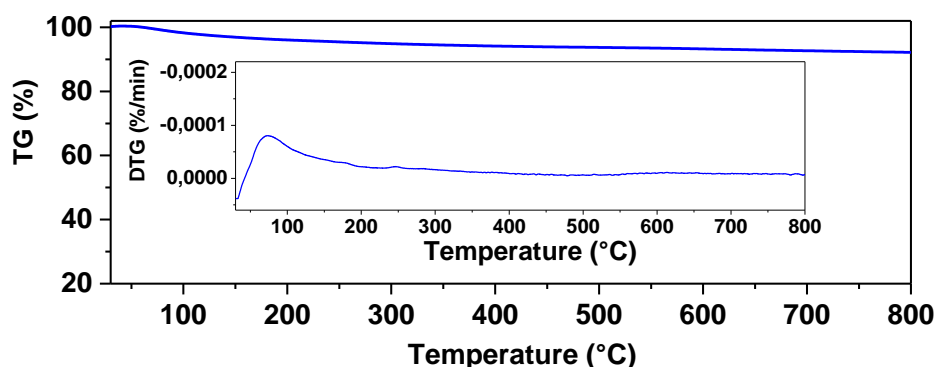


Figure 3: TG/DTG profiles of Pt/Al₂O₃ before the modification with NH₄BF₄.

FT-IR spectroscopy was used to analyze the chemical property of Pt/Al₂O₃ (Figure 4). The FT-IR profile showed a slight band at 3336 cm⁻¹ assigned to the stretching vibration of hydroxyl groups (Feng et al., 2014a). The band at 1640 cm⁻¹ can be ascribed to the typical deformation vibration of physically adsorbed water (Li et al., 2008). Finally, the profile showed a broad band at about 500 cm⁻¹, attributed to the Al–O bond of alumina (Li et al., 2008). In Figure 5, the FT-IR profile of Pt/Al₂O₃@NH₄BF₄ is shown. The profile evidenced the presence of new main bands at ~ 1485 cm⁻¹ and 720 cm⁻¹, probably due to the formation of aluminum borate (Feng et al., 2014a). These results confirmed the modification of Pt/Al₂O₃ with NH₄BF₄.

Acidities for Pt/Al₂O₃@NH₄BF₄ sample were monitored by FT-IR pyridine adsorption (Figure 5). Firstly, physically adsorbed pyridine was outgassed at 300°C in nitrogen flow for 3 h. The bands at 1445, 1579, 1597, and 1617 cm⁻¹ were ascribed to pyridine species adsorbed on Lewis acidic sites (Burtin et al., 1987; Morterra and Magnacca, 1996). The band at 1495 cm⁻¹ was assigned to the combined Brønsted and Lewis acid sites. Furthermore, the bands at 1545 cm⁻¹ and 1646 cm⁻¹, respectively, due to the pyridine adsorbed on Brønsted acidic sites, confirming the presence of Brønsted acidic sites (Feng et al., 2014b).

The surface composition of Al₂O₃ is responsible for the surface acidity of the catalyst, the surface of Al₂O₃ was covered with hydroxyl groups bound to sites of various geometries. As reported by Knözinger and Ratnasamy (1978), the surface composition/structure of alumina can be described by five types of surface sites.

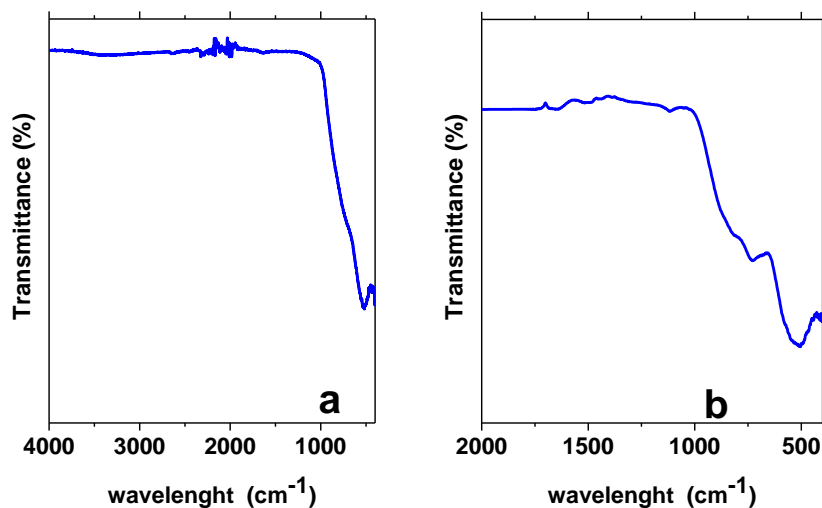


Figure 4: FT-IR spectrum for Pt/Al₂O₃ before (a) and after (b) the modification with NH₄BF₄.

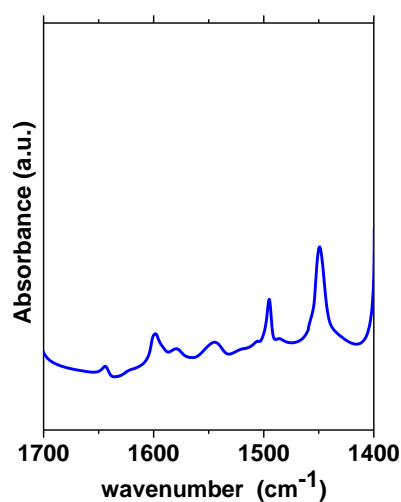


Figure 5: FT-IR spectrum of adsorbed pyridine on Pt/Al₂O₃ modified with NH₄BF₄. The sample is shown after exposure to pyridine and then treated under vacuum for 3 h.

In Figure 6, the mechanism explaining the formation of Brønsted acid sites on the alumina surface was shown (Feng et al., 2014a). -OH group, which can be bounded to two tetrahedral or octahedral aluminum atoms is also depicted. Fluorine modification replaces oxygen groups located on alumina atoms with strong electronegative F atoms. In the meantime, electrons from neighboring atoms were withdrawn leading to a decreased electron cloud density of -OH groups and allowing a much easier proton release, which improves Brønsted sites' acidity (Feng et al., 2014a). Boron atoms form B-O-Al are bound with under-coordinated aluminum.

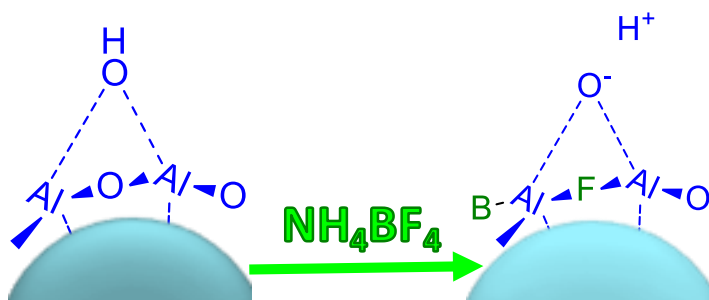


Figure 6: The schematic mechanism for the formation of Brønsted acid sites on the catalyst surface.

3.2 Electrochemical methanol conversion

The electrocatalytic activity towards MOR of the synthesized nanomaterial was tested in a 0.5 M H₂SO₄ and 2 M CH₃OH solution and the resulting CV response at 50 mV/s is shown in Figure 7a, in comparison with the controlled experiment. The sample exhibits low onset potentials (0.04V vs. SCE), indicating that CH₃OH oxidation reaction requires low energies to start.

The I_f/I_b ratio, the ratio between the peak current density in the forward scan (I_f) and the peak in the backward scan (I_b), was also evaluated. By providing a comparison of methanol oxidation with the oxidation of the intermediate carbonaceous species tightly absorbed on the catalyst, it is a reliable parameter to assess catalyst resistance to poisoning (Liu et al., 2017). The value obtained for Pt/Al₂O₃@NH₄BF₄ catalyst is of 2.14, proving a high tolerance towards CO poisoning (Tloroi and Yasuda, 2005).

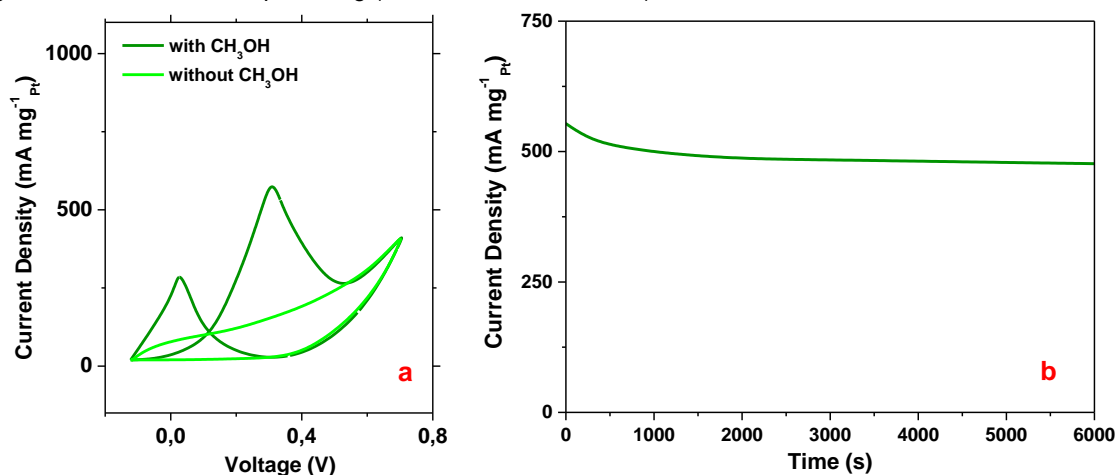


Figure 7: Cyclic voltammograms over Pt/Al₂O₃ modified with NH₄BF₄ in 0.5 M H₂SO₄ solution in the absence and presence of 2 M CH₃OH, at a scan rate of 50 mV/s (a). Chronoamperometry curve of Pt/Al₂O₃ modified with NH₄BF₄ in acid solution at 0.30 V (vs. SCE). Electrolyte: 0.5 M H₂SO₄ + 2 M CH₃OH (b).

At a voltage of 0.30 V (vs. SCE) chronoamperometry measurements were performed, as can be seen in Figure 7b. These measurements enabled evaluating the catalyst activity as time increased, showing that the current density decreases slightly and still remains at 476 mA/mg_{Pt} up to 6000 s.

As far as the literature is concerned (Sarno et al., 2019b), little or no effort has been dedicated to the evaluation of the electrode stability in comparison with Pt/C based material. However, the results of this paper demonstrate the feasibility of Pt/Al₂O₃ modified with NH₄BF₄ as stable electrocatalyst, highlighting the role of Pt single atom, for methanol electrochemical activation, supported on Al₂O₃, by the special surface properties, in enhancing the electrode activity. On the other hand, the excellent performances expressed by the catalyst developed in this work can be ascribed also to the high chemical and morphological control of the catalyst obtained and the key role of NH₄BF₄ surface modification allowing to obtain an improved amount of Brønsted acid sites on the catalyst framework, facilitating the flow of protons (Ueda et al., 2000) and the cleansing of the catalyst surface by minimizing the formation of intermediates as CO_{ads}.

4. Conclusions

An enhanced catalyst, for the efficient electrochemical oxidation of methanol based on Pt single atoms dispersed on Al₂O₃, was prepared. TEM analysis revealed the morphology of the nanomaterials, which are constituted of small nanoparticles of Al₂O₃. The synthesized nano-electrocatalyst was tested towards MOR, showing among the stronger poisoning resistance ever reported in literature. The excellent behaviour of our nanocatalysts can be attributed to a combination of aspects. The small Al₂O₃ nanoparticles, characterized by special surface properties, allow for electrode wettability, Pt single atoms inclusions permit efficient methanol activation and oxidation, and the key role of the Brønsted acid sites for avoiding catalyst poisoning.

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