Interfacial-redox interaction of NO_3^- and NO_2^- species over Pt nanoparticles supported on WO_3-ZrO_2-C

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Abstract: The reduction of NO_3^- and NO_2^- was carried out on platinum nanoparticles supported on carbon Vulcan (10 wt% Pt/C), as well as on the Pt/WO_3-ZrO_2-C (ZrO_2 25 wt%; WO_3 5 wt %, C 50 %wt) samples. The support was synthesized by the Coprecipitation method. Subsequently, platinum was incorporated to C and WO_3-ZrO_2-C supports by inert atmosphere impregnation method. These catalysts were evaluated using cyclic voltammetry. It was found a higher reduction current in Pt/WO_3-ZrO_2-C than in Pt/C in both reactions. Therefore, the oxide matrices are considered for good supporting and increasing the catalytic activity of the platinum nanoparticles.

Keywords: Enviromental catalyst, Electrocatalysts, Tungstated zirconia.

1. Introduction

The contamination of aquifers by nitrate and nitrite species caused mainly by the application of nitrogen-based fertilizers in intensive agriculture and effluent of nuclear water, poses a potential threat to human health [1]. Since it has been found that the human body reduces nitrates to nitrites, which produce methemoglobinemia (known as "blue baby syndrome") and transformed to nitrous amine which is a carcinogenic precursor. For this reason, the World Health Organization (WHO) recommends the limit of nitrates and nitrites in water as 10 ppm and 0.003 ppm respectively [2]. Therefore, the control and reduction of the NO_3^- and NO_2^- ion is evident. An alternative to solve this problem is the electrochemical reduction of the species mentioned, which has been studied on different materials that contain platinum nanoparticles [1]. On the other hand, the understanding and control of the properties of the WO_3-ZrO_2 catalysts has been a topic of interest for the last three decades, with a focus on discovering the relationship between the catalytic activity and the molecular structure of the surface acid sites [3]. In addition, low operating temperature, resistance to corrosion, good regeneration ability and excellent chemical and thermal stability in oxidant, reducing and neutral atmospheres are desirable characteristics in industrial applications [4].

2. Experimental

The catalyst was prepared by the coprecipitation method with different loads (25 wt, 25 wt%, 50%) of tungsten, zirconia and carbon Vulcan from zirconyl chloride ($ZrOCl_2xH_2O$), ammonium metatungstate (NH_4 $6W_{12}O_{39}\cdot xH_2O$) and carbon Vulcan (XC-72R). Briefly, all precursors were mixed by using NH_4OH as precipitating agent. After precipitation, the material was kept at 80 °C for 16 h. Subsequently, Pt nanoparticles were added by inert atmosphere impregnation method, with a 10 wt% Pt of the total support. Finally, the catalysts were washed and dried at 80 ° C for 12 h. The catalyst Pt/C was also prepared by inert atmosphere impregnation, with a 10 wt% Pt and 90 wt% carbon Vulcan XC-72R.

3. Results and discussions

Figure 1 and 2 show scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDS) analysis of Pt/WO_3-ZrO_2-C and Pt/C respectively. These figures clearly reveal the porosity of the catalyst that increase its specific area and facilitates the diffusion reactants. The analysis EDS (Table 1) was realized to know Pt load and normalize the current and just like that find effect of the WO_3-ZrO_2-C in the reaction of reduction of NO_3^- and NO_2^-. Figure 3 compare the profiles current vs potential (i-E) of Pt/C and Pt/WO_3-ZrO_2-C in 0.5 M NaOH. These profiles have four zones linked with catalytic activity, 1) sub-potential region of hydrogen deposition, 2) metal oxide formation and 3) its reduction (Box 1, 2 and 3, respectively). In zone four a peak it was observed, which can be attributed to electro-adsorption of H^+ on WO_3 or ZrO_2, which is not observed in Pt/C. Figure 4 show the reduction process of Pt/C and Pt/WO_3-ZrO_2-C in presence of $NaNO_3$. The reduction of NO_3^- ion (zone 2) it was 20% more intense at Pt/WO_3-ZrO_2-C catalyst compared to the Pt/C catalyst. In addition, it was not observed an inversion potential (zone 1) in Pt/WO_3-ZrO_2-C catalyst, unlike the Pt/C catalyst. So that, NO_3^- did not adsorbs on the interface during the anodic scan, that confirm the increment in the faradic current. On the other hand, in the nitrite-reduction (Figure 5) process the current on Pt/C and Pt/WO_3-ZrO_2-C increases in comparison with the nitrates-reduction (Figure 4). A possible reaction pathway is presented in equations (1-2)

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \tag{1}$$

$$2NO_2^- + 6e^- + 8H^+ \rightarrow N_2 + 4H_2O \tag{2}$$

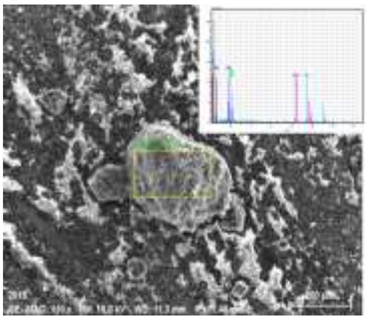


Figure 1. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDS) of Pt/WO_3-ZrO_2-C.

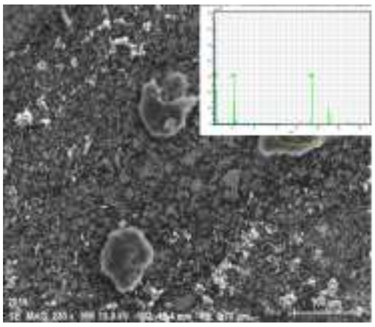
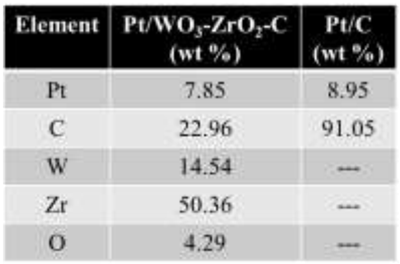


Figure 2. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDS) of Pt/C.



Element	Pt/WO_3-ZrO_2-C (wt %)	Pt/C (wt %)
Pt	7.85	8.95
C	22.96	91.05
W	14.54	---
Zr	50.36	---
O	4.29	---

Table 1. Elementary analysis according to EDS

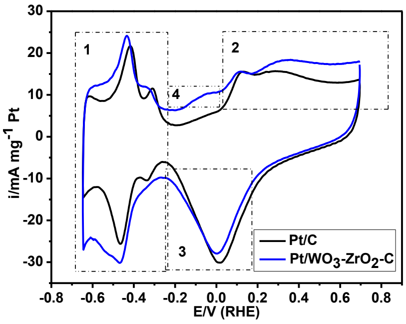


Figure 3. i-E profiles of the Pt/C and Pt/WO_3-ZrO_2-C. Supporting Electrolyte NaOH 0.5 M. Scan Rate 20 mV/s.

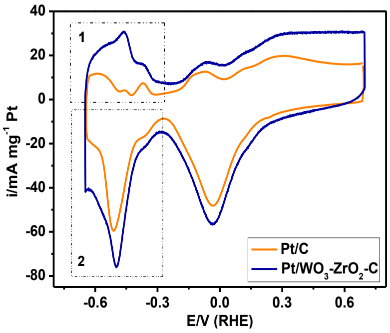


Figure 4. i-E profiles reduction of NO_3^- in Pt/C and Pt/WO_3-ZrO_2-C. Supporting Electrolyte 1 M $NaNO_3$ and 0.5 M NaOH. Scan Rate 20 mV/s.

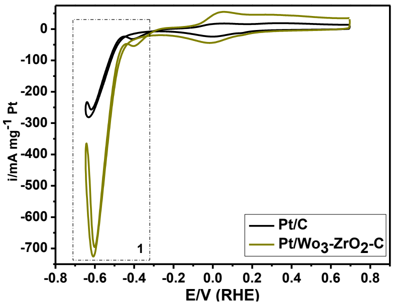


Figure 5. i-E profiles reduction of NO_2^- in Pt/C and Pt/WO_3-ZrO_2-C. Supporting Electrolyte 1 M $NaNO_2$ and 0.5 M NaOH. Scan Rate 20 mV/s.

4. Conclusions

In this work, it has been demonstrated that the electocatalytic reduction of NO_3^-, NO_2^- (in alkaline medium) can be enhanced by supporting Pt nanoparticles onto the mixed metal (W, Zr) oxide matrix fabricated as composite with carbon. Significant increment of faradic currents (measured under steady-state conditions at room temperature) was observed. The enhancement effects should be attributed to features of the mixed metal oxide support such as i) porosity and high population of hydroxyl groups (due to presence of ZrO_2), ii) high Bröensted acidity of sites formed on WO_3-ZrO_2-C, iii) fast electron transfers coupled to unimpeded proton displacements, as well as strong metal-support interactions between Pt and metal oxo species.

References

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