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Innovative Deposition of Platinum-Graphene on Alumina for Passive Autocatalytic Recombiners to Improve Nuclear Safety

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1. Introduction

The generation of hydrogen (H_2) in nuclear facilities under severe accident conditions is a critical issue, triggering substantial risks for safety. This challenge becomes particularly relevant in gas mixtures that include air and H_2, with the latter's volumes ranging from 6% to 30%. One strategy to address this problem is the use of Passive Autocatalytic Recombiners (PARs), which play a crucial role in mitigating the risk of hydrogen-induced explosions [1]. Installing PARs inside the containment can significantly reduce the chances of H_2 explosion.

The effectiveness of PARs is anchored in the catalyst's ability to recombine hydrogen with oxygen on active catalytic surfaces, resulting in the generation of water vapor and heat [2]. Catalysts are often composed by active materials, such as platinum, deposited on materials like stainless steel, alumina, and silica. Despite advancements, the practical application of these catalysts faces challenges, including the need to reduce production costs and enhance operational stability, particularly due to water inactivation, especially under high humidity conditions in the reactor containment during severe accident scenarios [1].

In the quest for solutions to water inactivation, research has explored the use of hydrophobic materials. For instance, grafting perfluorooctyltriethoxysilane (FAS) has shown to enhance the activity of traditional Pt-Al_2O_3 catalysts [2]. Moreover, the addition of hydrophobic polymers as a coating on the catalyst is being studied. Graphene, known for its hydrophobic properties when only a few layers thick, has been the subject of study to overcome the mentioned challenges. In recent works, Gomes and collaborators [3, 4] successfully grew graphene flakes on insulating surfaces like fiberglass and boron nitride using non-thermal plasma. This approach resulted in a material with few layers and structural hexagonal defects, standing out for its simplicity, low cost, and scalability. These characteristics make it a promising candidate for producing effective hydrophobic catalysts to be applied in PARs. In the scope of this study, the relationship between the amount of platinum and graphene precursors obtained through the non-thermal plasma method in a single step was explored. These elements were supported on alumina aiming at hydrogen reconversion into water, with potential applications in nuclear safety devices.

2. Methodology

The deposition process of platinum-graphene on Al_2O_3 was carried out using a non-thermal plasma generator coupled to a reaction vessel, where an arc is generated (Fig. 1). In this reactor, employing cyclohexane (Aldrich) in different ratios (5:1, 10:1, and 20:1 by mass relative to alumina), along with appropriate amounts of platinum precursor ($H_2PtCl_6 \cdot 6H_2O$) to achieve different Pt compositions (0.5%, 1%, and 2% by mass relative to alumina) as starting material, a 60 kV arc is applied with a flow of $N_{2(g)}$ between 316L steel

electrodes until to finish the liquid reagents.

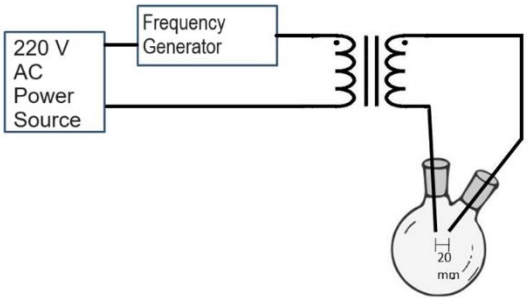

Figure 1: Non-thermal plasma generator coupled to a reaction vessel with cyclohexane for platinum-graphene production.

The dried material is characterized using scanning electron microscopy (SEM) Jeol JSM-6701F. X-ray diffractions (XRD) were obtained with a Miniflex II diffractometer, using Cu Kα radiation at 0.15406 Å, configured in a 2θ range from 2 to 90°, with a scanning speed of 2 min^{-1}. Raman spectra were collected using a Horiba Scientific MacroRam Raman spectroscopy device with a 785 nm laser. Wettability tests were performed by water retention in the material, where the catalyst is immersed in ultrapure water for 10 minutes, allowed to drain for 20 minutes at room pressure and temperature, weighed again, and from there, the mass gain is calculated. Catalyst activity tests were conducted using a device in which 2.0 g of sample was distributed in a closed compartment with a length of 10 mm and a radius section of 20 mm, crossed by a constant flow of 170 mL min^{-1} of H_2 and 100 mL min^{-1} of O_2. Activity was monitored over 60 minutes after gas signals stabilized using a quadrupole mass spectrometer, 200 a.m.u. DaQMS 200 M1, Prisma, Pfeiffer equipped with a continuous dynode secondary electron multiplier/Faraday cup detector and sensitivity of 200 A $mbar^{-1}$.

3. Results and Discussion

The scanning electron microscopy images (Figure 2a) reveal a change in the material's morphology, where materials with lower platinum content exhibit a smoother texture compared to a more robust appearance in materials with 2% Pt. Additionally, surface roughness and defects are noticeable, likely caused by the facilitated exfoliation process in this synthesis configuration [4]. Platinum, characterized by the brighter spots, becomes more pronounced with an increased amount of graphene precursor, indicating that the metal prefers to stay on the surface with the rising amount of cyclohexane, without being concealed beneath graphene layers. Moreover, the size of the clusters is more apparent, probably due to a larger amount of liquid allowing reduced platinum particles to aggregate less during the formation of the graphene-like structure on alumina.
In Figure 2b), the X-ray diffraction (XRD) patterns of pure alumina, alumina coated with graphene, and alumina with graphene and platinum are presented. Materials containing graphene exhibit peaks at approximately 2θ ~ 22.3° and 24.6° [3], corresponding to the crystalline planes (002) and (100) of carbon. The existence of these two planes indicates the presence of graphene. Although the peaks related to the face-centered cubic structure of platinum (~39, 46, and 68º) overlap with the peaks of Al_2O_3, the presence of this noble metal can be observed through Raman spectroscopy (Figure 2c), marked by the band center at 603 cm^{-1}. Additionally, bands centered at 1320, 1585, and 1620 cm^{-1} are identified, corresponding to the D1, G, and D2 bands of carbon, respectively [5]. In the literature, the Raman intensity ratio between the D and G bands (I_{D1}/I_G) is a parameter used to characterize the degree of disorder in graphene. It is noted that for graphene-Al_2O_3 and Pt1% - Graphene Precursor (GP) 40 – Al_2O_3, these ratios are 2.25 and 1.62, respectively. In both cases, this value indicates the presence of defects in the structure, suggesting a certain amount of disorder in the graphene structure [5].

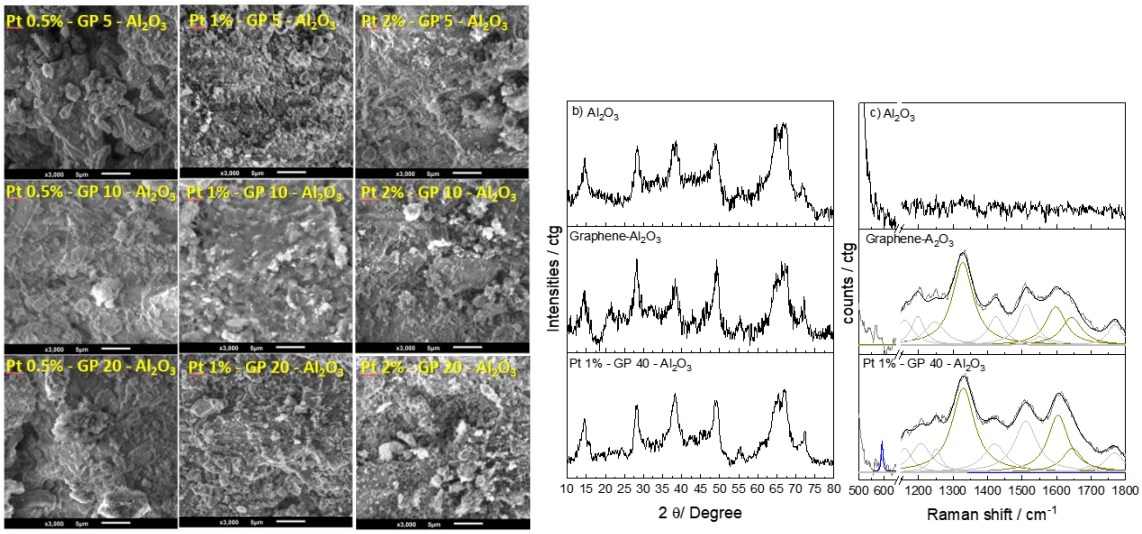

Figure 2: a) SEM images of Pt-GP (Graphene Precursor) – Al_2O_3 materials; b) X-ray diffraction patterns of Pt-GP-Al_2O_3; c) Raman Spectrum of Pt-GP-Al_2O_3 catalysts, in blue platinum band, and in dark yellow carbon bands.

The data obtained from wettability experiments (Table I) revealed that the increase in the amount of graphene precursor resulted in an increase in the wettability of the catalyst. This phenomenon may be associated with the formation of graphite nanoflakes on the material, in addition to graphene itself.

Table I: Wettability results.

Material	H_2O retention (% mass)
Al_2O_3	39.4
GP-Al_2O_3	2.3
Pt 0.5% - GP 5 – Al_2O_3	3.3
Pt 1.0% - GP 5 – Al_2O_3	2.8
Pt 2.0% - GP 5 – Al_2O_3	2.8
Pt 0.5% - GP 10 – Al_2O_3	10.8
Pt 1.0% - GP 10 – Al_2O_3	7.6
Pt 2.0% - GP 10 – Al_2O_3	5.3
Pt 0.5% - GP 20 – Al_2O_3	7.5
Pt 1.0% - GP 20 – Al_2O_3	10.1
Pt 2.0% - GP 20 – Al_2O_3	9.6

After stabilizing the flow, the passage of hydrogen through the catalysts was measured using a mass spectrometer (Figure 3). It is observed that materials containing a higher amount of graphene precursors were more active, and the catalyst with Pt 1.0% ~~-~~showed the highest conversion of hydrogen into water.

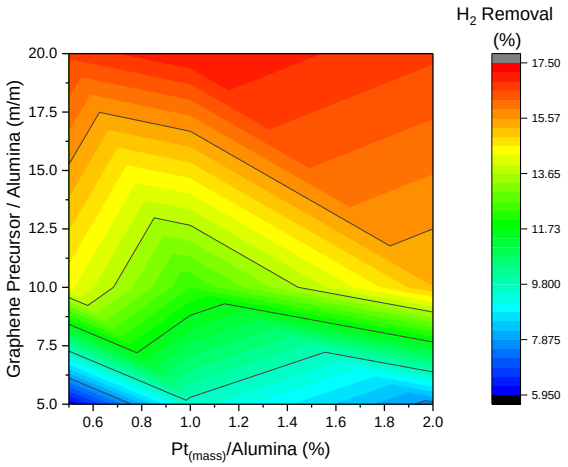

Figure 3: Hydrogen removal activity in a flow as a function of the composition of the Pt-GP-Al_2O_3 catalyst.

4. Conclusions

The successful implementation of the platinum-graphene deposition process on alumina using a non-thermal plasma generator revealed significant modifications in the morphology and structure of the resulting catalysts. Scanning electron microscopy analysis indicated a smoother texture in materials with lower platinum content. Additionally, the presence of graphene was confirmed by XRD patterns. Wettability experiments demonstrated that an increase in the graphene precursor amount contributed to higher wettability of the catalyst, possibly due to the formation of graphite nanoflakes on the material. Through Raman spectroscopy, the presence of platinum was identified, indicating that this noble metal remained predominantly on the catalyst's surface. When evaluating the hydrogen removal activity in flow, it was observed that catalysts with a higher amount of graphene precursors exhibited greater activity, with the Pt 1.0% containing catalyst standing out with the highest conversion of hydrogen into water. The relationship between the platinum amount and graphene precursors was explored, revealing a direct influence on the effectiveness of the catalyst for hydrogen reconversion. These results suggest promising applications of these catalysts to improve the performance of PARs to mitigate the risk of hydrogen accumulation in nuclear facilities under severe accident conditions, enhancing nuclear safety.

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