CHARACTERIZATION OF Pd BASED CATALYSTS SUPPORTED ON GRAPHENE

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Abstract

This contribution studied Pd based catalysts supported on graphene derivatives (reduced graphite oxide and CeO_2-rGO hybrid), synthesized under hydrothermal conditions, evaluating the thermal stability and interactions metal-support. XRD of 1Pd/rGO and 1Pd/5Ce/rGO showed diffraction lines corresponding to Pd^0, suggesting an intimate contact between Pd and rGO. The Pd^0 presence after synthesis is unusual in catalysts prepared by conventional methodologies. The behavior described here can be attributed to a strong interaction between Pd and oxygenated groups of graphite oxide (precursor) under hydrothermal synthesis. In contrast, XRD pattern and Raman Spectrum of 1Pd/5Ce/rGO denote CeO_2 has segregated over the support without appreciable interaction. Concerning to the thermal stability, both samples rGO and 1Pd/rGO presented high thermal resistance (> 500°C) while upon Ce addition the temperature of degradation decreased drastically (~320°C). Raman Spectroscopy of rGO based sample showed the hydrothermal treatment lead to defects presence which is beneficial for catalysis purposes.

Keywords: Graphene catalysts, Pd, hydrothermal, CO_2 hydrogenation

1. Introduction

Graphene is a promising material for different technological areas due to its unique properties such as high conductivity, high mechanical strength, chemical stability, to mention few[1,2]. The high surface area, the presence of intrinsic structural defects combined with the chemical stability make graphene very attractive as catalysts support. The catalytic properties of graphene supported metals have been investigated for several reactions[2]. The strong interaction between oxygenated groups and metal provides a better metallic dispersion with a greater stability towards sintering. The present contribution investigated Pd catalyst supported on reduced graphite oxide (rGO), 1Pd/rGO, and on CeO_2-rGO hybrid, 1Pd/5Ce/rGO, evaluating the thermal stability and interactions between Pd, CeO_2 and rGO. Pd was chosen as an active phase due its excellent catalytic properties in hydrogenation reactions, being an effective candidate for the CO_2 hydrogenation.

2. Experimental

2.1. Catalysts Synthesis

Graphite oxide (GO) was synthetized by oxidation of graphite powder (Sigma-Aldrich) in according to the modified Hummers method[3]. Graphene (reduced graphite oxide, rGO) was synthetized through the hydrothermal reduction of GO at 180°C (16 hours)[3], using a Teflon lined autoclave.

Pd and Ce load were 1%wt and 5%wt, respectively.

2.2. Sample Characterization

The N_2 adsorption measurements were carried out at -196°C on NOVA 1100 from Quantachrome Instruments. The samples were initially dried at 100°C during 2 hours. Afterwards, the catalysts were outgassed at 300°C for 2 hours. Surface areas were calculated from adsorption isotherms by applying the BET theory. XRD patterns were recorded on a D8Focus/Bruker diffractometer using Cu-Kα radiation (Ni filter, $\lambda K\alpha_1$ = 1.5406 Å). The diffraction patterns were obtained at the room temperature over 2θ range from 10° to 100° with 2θ step of 0.02.

Thermal analysis were carried out in a TA analyser (STA 443 Jupiter/Netzsch) by heating the sample from the room temperature until 800°C (5°C/min) under air flow. The exit gas of TGA analysis was monitored by a Mass Spectrometer (QMS 403 D Aeolos/Netzsch).

Raman spectra were recorded using a Horiba Scientific spectrometer (Laboram HR Evolution model) with wavelength of 514 nm at the room temperature.

3. Results and Discussion

The X-Ray diffraction patterns of the samples were collected after synthesis and drying at 60°C. The high oxidation of graphite was verified by the presence of a sharp peak at d-spacing 0.75 nm, which reveals a restructuring of graphite sample through the intercalation of oxygenated groups (hydroxyls, epoxy, carboxylic, others) in a well-organized crystalline structure[2]. XRD pattern of the reduced graphite oxide exhibited a broad peak at d-spacing maximum of 0.36 nm, indicating a conversion of GO to a reduced graphite oxide by a removal of most of oxygenated groups. A riddance from oxygenated groups results in a domination of Van der Waals forces, leading to a modification of the layers stacking of GO. XRD pattern of the catalyst 1Pd/rGO showed that the reduced graphite oxide structure was preserved. Furthermore, the pattern exhibited a low intensity peak at d-spacing 0.23 nm corresponding to Pd^0. The appearance of Pd^0 suggests a strong interaction between Pd and reduced graphite oxide. Upon Ce addition to the sample (1Pd/5Ce/rGO), the pattern exhibited features characteristic of ceria with fluorite structure. The peaks related to ceria were sharp and intense, indicating a weak interaction with rGO. It is interesting to note that in both catalysts Pd^0 peak was weak and broad, suggesting, as expected, a high metal dispersion.

The defects presence in these samples was investigated by Raman spectroscopy which disclosed an increase of the defects concentration upon graphite oxidation, as indicated by D band appearance at 1584 cm^{-1}. This band is characteristic of defects and disorder in grahene lattice[4]. Upon reduction of GO to rGO it was detected a small decrease in the ratio of intensities of D and one of the main graphite, G, bands (ID/IG), complemented by a G band displacement from 1584 to 1611 cm^{-1}. The ID/IG ratio is widely used as a measure of the disorder and the average size of sp^2 domains[3]. As already pointed out by Siamaki et al[4], defects are undesirable for graphene applications in electronic devices but they are useful for catalytic purposes as they facilitate the interaction of reactant molecule with the solid surface. Raman spectrum of 1Pd/5Ce/rGO exhibited vibrational mode attributed to ceria (459 cm^{-1}). Heterogeneous distribution of ceria in the sample was evidenced by Raman spectroscopy. This result corroborates with XRD measurements, denoting the ceria phase segregation in the catalyst´s structure.

The catalyst´s stability was investigated under air atmosphere (Figure 1) using thermogravimetric analysis coupled with a mass spectrometer (TG/MS). The monitored mass, m/e, were 18, 29 and 44 corresponding to H_2O, CO and CO_2. According to mass spectra, H_2O and CO_2 were detected. The derivative of the weight loss curve (Figure1) shows two regions of

intense weight loss for GO, characterized by the peaks centered at 214 and 508°C. The first peak can be attributed to the decomposition of oxygenated groups[5], while the second peak is associated with the thermal degradation of graphene oxide. Reduced graphite oxide sample showed an increased thermal stability, as evidenced by the TG peak centered at 549°C.
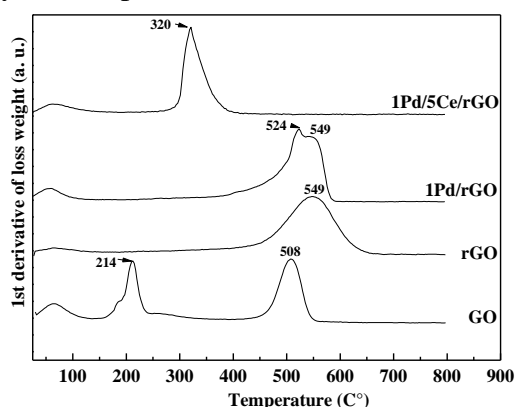

Fig. 2. Stability comparison of the samples by the first derivative of the loss change. TG/MS analysis were performed under airatmosphere (25-800°C; 5°/min).

The addition of Pd to the rGO sample resulted in a broad peak with a slightly reduced degradation temperature, as compared to not modified rGO sample. The asymmetric and split character of the TGA peak shape denotes a multicomponent peak structure originated, most probably, from different forms of carbon. Although Pd is known to be effective in catalyzing combustion reactions[6], its effect over rGO degradation, opposite to what might be expected, was small, and did not affect significantly the thermal stability of the sample. As a matter of the fact, the role of Pd in combustion reactions is related to its oxidation state which also depends on the used support. Indeed, XRD results indicate the formation of Pd^0 which is not considered the active phase in oxidation reactions by most of the studies[7]. Upon ceria addition to the sample, a striking acceleration of the thermal degradation of the sample promoted by the oxygen storage ability of ceria was observed. Possible interactions between ceria and Pd can also contribute to this process.

4. Conclusions

The hydrothermal method used in this study allowed an efficient reduction of GO to rGO. The obtained results suggest an intimate interaction between Pd and rGO. On the other hand, the ceria-rGO binding was weak, resulting in the ceria segregation over the support. With respect to the catalyst stability, the ceria addition to Pd/rGO decreased drastically the degradation temperature of the catalyst. This behavior can be associated to the high ceria oxygen storage capacity. Nevertheless, this shortage does not preclude the use of Pd/5Ce/rGO system in various catalytic applications. The chemical stability of the studied catalysts envisions them as promising candidates for catalytic conversions such as the CO_2 hydrogenation.

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