

From Graphite Oxide to Graphene-like Sheets via Thermal Reduction: Kinetic Mechanisms

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Introduction

Graphite oxide (GO) has been known since the 19th century but it has recently re-emerged as an intensive research area due to its importance in obtaining large-scale graphene materials, afforded by the chemical or thermal reduction of GO, among others. Chemical reduction involves the use of reducing agents such as hydrazine, hydroquinone and NaBH₄ while the thermal treatment at elevated temperatures avoids the use of these hazardous chemicals and provides a rapid and efficient method to produce large amounts of graphene-like sheets. Deoxygenation of GO upon chemical or thermal reduction has been systematically studied in the past, where the restoration of C=C bonds and the decrease in the number of C-OH, C-O-C, COOH groups have been experimentally and theoretically determined [1-3]. However, deoxygenation is not completed after reduction by which residual amounts of oxygen vary depending on the reduction process (temperature, atmosphere, treatment). Studies by molecular dynamics simulations showed that these residual amounts of oxygen in reduced GO are also dependent upon the initial oxygen concentration and the hydroxyl/epoxide ratio [2]. Furthermore, since a great variety of GOs with variable chemical composition and interlayer spaces can be obtained via the synthesis methods that comprises that of Brodie, Hummers and Staudenmaier methods, the composition and, therefore, the chemical-physical properties of reduced GO, can be extensively different.

In spite of repeated efforts, the mechanisms involved in the thermal reduction of GO are far from clear and no predictions can be made on the final properties of the reduced GO. For that reason, intensive studies on the thermal reduction of GO are of great importance, especially when combining different experimental techniques in order to provide structural and compositional information. Following this idea, in the present study, temperature- and time-resolved x-ray diffraction (XRD) and thermogravimetric analysis (TGA) are used to monitor the structural changes of GO upon dynamic (non-isothermal) and static (isothermal) modes. To gain further insight in the reduction reactions taking place, simultaneous TGA/mass spectrometry (MS) experiments are also conducted in both modes. Isothermal TGA is run at various temperatures in the 120-220 °C range, enabling the establishment of the kinetic mechanisms involved in the thermal reduction of GO. Moreover, the kinetic mechanisms of several GO prepared by the different synthesis methods are compared.

Kinetic experiments

Figure 1 shows the weight loss rate of a Brodie-based GO (from natural graphite) as a function of weight percent. In this representation, it is very apparent that two different mechanisms for weight loss exist, each dominating a particular range. The best fitting for mechanism I was accomplished with a two-dimensional diffusion model whereas for mechanism II an autocatalytic model was found very adequate. These results, although contrast with previously published second order kinetics by both McAllister et al. [1] and Jung et al. [3], are in agreement with a further experiment where GO was obtained from

synthetic graphite (Figure 2a). Notable differences were found in mechanism I for the Brodie-based GO obtained from both synthetic and natural graphite, in which diffusion mechanism occurs in different weight percent ranges. Figure 2 shows the dependence of the reduction kinetic mechanisms on the GO synthesis method. Whereas the weight loss rate for Brodie-GO fitted to both diffusion and autocatalysis, as above mentioned, that for Hummers- and Staudenmaier-GO fitted to n-order kinetics only at highest weight losses. These results account for the importance of both the GO synthesis method and starting graphite in determining the kinetic behavior of thermal reduction.

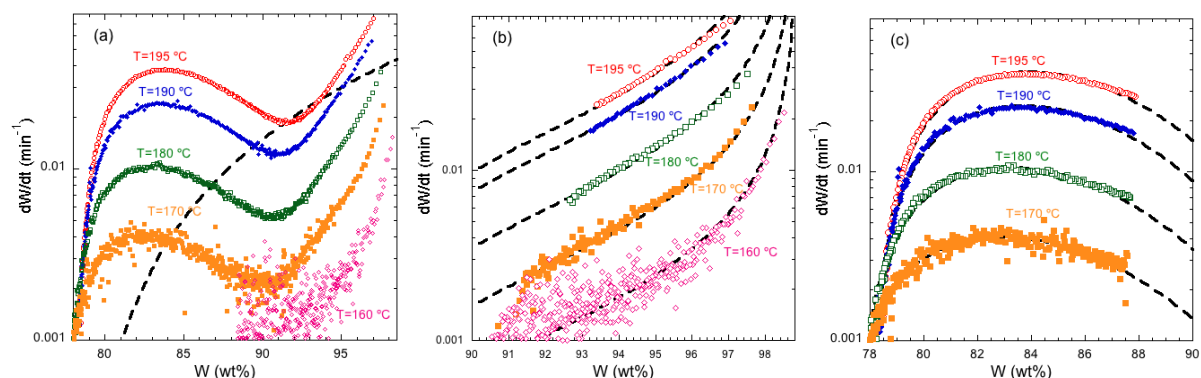


Figure 1. Isothermal TGA experiments. Weight loss rate (dW/dt) of Brodie-based GO (from natural graphite) as a function of the percentage weight loss (W) at different temperatures. a) Whole process. Dashed line depicts a second-order mechanism. b) Mechanism I: fitting curves with a two-dimensional diffusion model and c) Mechanism II: fitting curves with an autocatalytic model. Reported in reference [4].

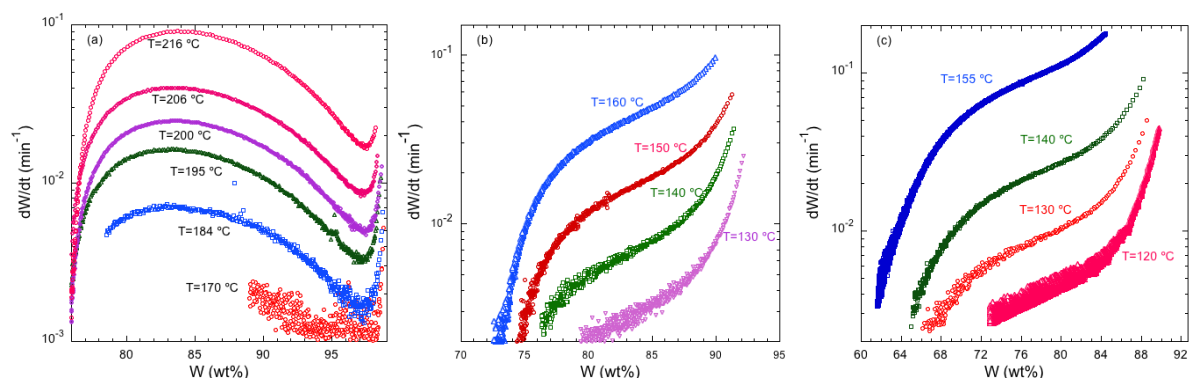


Figure 2. Isothermal TGA experiments. Weight loss rate (dW/dt) of GO (from synthetic graphite) obtained from a) Brodie, b) Staudenmaier c) and Hummers –based methods as a function of the percentage weight loss (W) at different temperatures.

Conclusions

The thermal reduction studies for a series of GO obtained from the Brodie, Staudenmaier and Hummers methods revealed new experimental evidences of the kinetic mechanisms involved. While combined dynamic TGA and temperature-resolved XRD enabled the monitoring of the structural changes taking place in GO during the thermal reduction, isothermal methods were more effective. Combined isothermal-TGA and time-resolved XRD showed that two distinct and well-resolved mechanisms were involved in the thermal reduction of Brodie-based GO, 2D-diffusion and autocatalysis; whereas n-order kinetics were observed for Hummers- and Staudenmaier-based GO.

References

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