

UNDERSTANDING THE ACIDITY OF GRAPHENE OXIDE BY MICROCALORIMETRY AND IN SITU FTIR STUDIES

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Graphene oxide (GO) had been widely investigated as an alternative for acid solid catalyst. Its structure was deeply studied trying to understand the source of its acidic properties. Many hypotheses have been suggested. The most common one in the literature is related to a synergy between numerous oxygenated functional groups created in the GO sheet during its synthesis via Hummer modified method. However, we have suggested in our team that GO Brønsted acidity might originate from the presence “free” protons explained by the delocalization of negative charges of the counter anions in the conductive GO sheets [2].

In this work, we aimed to understand the influence of the thermal pretreatments under vacuum on the GO superficial oxygenated groups and on its acidic properties. That was done using several characterization methods: FTIR of Pyridine (Py) adsorption and D₂O exchange, calorimetry of NH₃ adsorption and XPS. First, XPS and FTIR demonstrated that for $T < 200^\circ\text{C}$, GO didn't lose its oxygenated groups. However, 250°C is observed to be a pivotal temperature where GO becomes a non acidic material after the complete removal of its oxygenated groups as seen by FTIR of Py adsorption (fig.1) and calorimetry of NH₃ adsorption. Calorimetric experiments performed on GO pre-treated within this T range ($100\text{--}200^\circ\text{C}$), consolidate also our earlier assumption about the presence of “free” protons since heat of NH₃ adsorption measured of $200\text{ kJ}\cdot\text{mol}^{-1}$ can be measured as a function of the thermal pretreatment. Such a high heat of ammonia adsorption was measured over 12-tungstophosphoric acid only, where the presence of protonated water clusters $\text{H}(\text{H}_2\text{O})_n^+$ was established by different techniques. Finally, D₂O exchanges were conducted comparatively over GO and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in order to evidence the presence of $\text{H}(\text{H}_2\text{O})_n$ species..

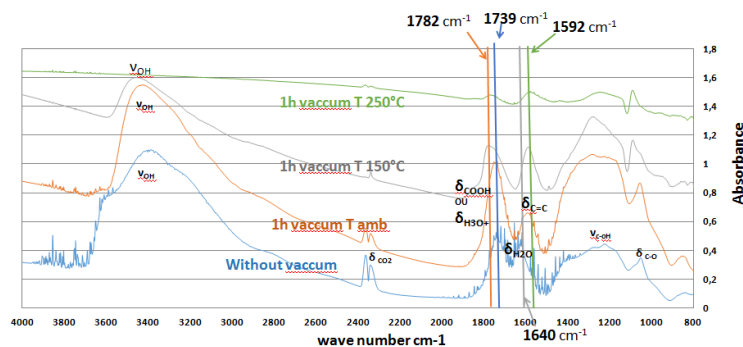


Figure 1. FTIR spectra of GO vacuum treated at T_{amb} , 150°C and 250°C

References:

- [1] V.C.Nguyen,, N.Q.Bui, P.Mascunan, T.T.H.Vu, P.Fongarland, N.Essayem, Appl.Catal.A,General. 552 (2018) 184.