Evidence for CH bond Weaking in Alkanes on Metal-Supported Graphene

Peter McBreen
Sonali Balasaheb Khomane, Tianchi Zhang
Laval University, Québec City, Québec, Canada G1V0A6
peter.McBreen@chm.ulaval.ca

We interpret vibrational spectroscopy data for molecules on metal-supported graphene (Gr) in terms of electron transfer from the molecule to graphene and electron-transfer from graphene to the molecule, at different loci in the adsorbate. The systems studied are *N*-heterocyclic carbenes (NHCs) on Gr/Pt and Gr/Ru. NHC ligands, of the general structure shown below, are now widely used to functionalize metal surfaces, given that they form layers that are highly robust under aggressive conditions. Recently, we provided strong evidence that they may also be used to functionalize metal-supported graphene. NHCs are strong electron donors and this property correlates well with our observations on the relative strengths of NHC bonding to Gr/Pt(111), Gr/Ru(0001), Gr/O/Pt(111) and Gr/O/Ru(0001) systems [1]. In addition to their so-called backbone structure, where the carbenic centre is located, NHCs display wingtip groups. For example, the structure shown below has *tert*-butyl wingtips. In our experiments, the wingtips are methyl, isopropyl or *tert*-butyl groups: they only contain sp^3 C-H bonds. The central result is that IR reflectance measurements show softened wingtip C-H stretching vibrations on interaction with Gr/Ru(0001). This observation is consistent with an electronic perturbation of the wingtip C-H orbitals. Ongoing DFT calculations dedicated to the C-H bond activation will be discussed. These studies provide new insight on the catalytic potential of graphene, on substrate activation of graphene, and on graphene mediated electron-transfer processes.

References

[1] Zhang, T.; Khomane, S. B.; Singh, I.; Crudden, C. M.; McBreen, P. H. J. Phys. Chem. C, *126* (2022)14430.

Figure 1: An *N*-heterocyclic carbene with tert-butyl wingtip groups