Covalent Chemistry of small molecules on supported 2D Materials

C. Papp[1]

[1] *Physikalische und Theoretische Chemie, Freie Universität Berlin, Arnimallee 22, 14195 Berlin, Germany*

Email: christian.papp@fu-berlin.de

Understanding the chemical reactivity of 2D materials such as graphene and hexagonal-boron nitride (h-BN) is of fundamental importance for obtaining tunable materials for devices and electronic applications, as well as for fundamental science to obtain general concepts for the chemistry on such materials. The talk will consider two main points.

First, the interaction of graphene and h-BN with oxygen and atomic hydrogen will be discussed in details and the results for the two substrates will be compared. While in the case of atomic hydrogen, graphene forms graphone, i.e. fully hydrogenated graphene, for h-BN hydrogen can bond and intercalate, depending on the exposure. Interestingly, graphene does not react with molecular oxygen, even when supplied with a high kinetic energy of 0.7 eV, while h-BN readily forms bonds to oxygen, intercalates or even reacts, depending on the substrate temperature. Further insights to the bonding and reaction mechanisms of hydrogen and oxygen are obtained from DFT calculations.

The second topic shows that the general knowledge gained can be used in the case of Moire patterend 2D materials for spatially defined functionalization. In the case of h-BN on Rh(111), such functionalization is especially interesting since the pores and wires show different reactivity towards functionalization enabling spatially defined modification of h-BN. This is shown for the spatially defined surface chemistry of bromine on the 2D materials h-BN and graphene. In the case of the h BN/Rh(111) nanomesh, we observed exclusive pore adsorption for low coverages, confirming the desired template effect. For graphene, no such selectivity was found. Bromine on h-BN/Rh(111) revealed a high temperature stability (desorption at ~ 640 K), indicating covalent bonding, and a thermally induced on-surface reaction. Bromine on graphene/Rh(111), on the other hand, desorbed already at ~ 250 K, which suggests physisorption. In both cases, the adsorption was reversible upon heating.