Surface Chemistry on 2D materials

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Understanding the chemical reactivity of 2D materials such as graphene and hexagonal-boron nitride (h-BN) is of fundamental importance for obtaining flexible and tuneable materials for devices and electronic applications, as well as for fundamental science to obtain concepts for the chemistry on such materials. We present a comprehensive study on the reactivity of h-BN with the small molecules hydrogen and oxygen. NEXAFS, XPS and DFT allow for a detailed understanding of the involved processes. Insights in the dehydrogenation reaction and reactions with oxygen at elevated temperatures are gained from TPD and TPXPS measurements.

For the reaction with hydrogen with h-BN on a Ni(111) a wide exposure range was investigated. Low hydrogen exposures lead to hydrogenation of h-BN; in contrast, intercalation of hydrogen between h-BN and the Ni(111) substrate occurs for high exposures. From temperature-programmed experiments, we conclude that the hydrogen covalently bound to h-BN is rather stable with a desorption temperature of 600 K, while intercalated hydrogen is desorbing already at 300 K. Further insight into the structural arrangements and the thermodynamics of the system is obtained by comparing our experimental results with extensive DFT calculations. Together with UPS measurements, the calculations provide detailed insight in the influence of hydrogenation on the electronic structure of h-BN. [1]

We find that the reaction of h-BN with molecular oxygen is an activated process, as additional energy needs to be supplied from a supersonic molecular beam. With a kinetic energy of 0.7 eV oxygen coverages up to 0.4 ML were achieved. Depending on the substrate temperature we find different surface processes. When the sample is at room temperature, we find that oxygen binds molecularly in a side-on geometry. At 400 K, intercalation becomes the majority reaction path and at even higher temperatures of 600 K etching of h-BN becomes the most favourable. Interestingly, graphene does not react with molecular oxygen under similar conditions, even when supplied with a high kinetic energy of 0.7 eV. Further insights to the bonding and reaction mechanisms of hydrogen and oxygen are obtained from DFT calculations.

The reaction of the two adsorbates, oxygen and hydrogen, on h-BN is also accessible and is followed *in situ*, showing a continuous change of the valence and core level spectra.

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[1] F. Späth, J. Gebhardt, F. Düll, U. Bauer, P. Bachmann, C. Gleichweit, A. Görling, H. P. Steinrück, and C. Papp, 2D Materials, 4 (2017) 35026.