Near Ambient Pressure reaction under graphene cover on Ni(111)

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Ni is a known catalyst for the Boudouard reaction which is favored by high pressure
We report here on a Near Ambient Pressure XPS study performed at Soleil Synchrotron using the Tempo Beamline.
If a bare Ni(111) sample is exposed to CO at a pressure P_{CO}~2 mbar, the growth of graphene can occur already at 550 K [1], a temperature significantly lower than the one (670 K) required for the growth by segregation of dissolved carbon. The direct growth can be explained in terms of Boudouard reaction ($CO+CO \rightarrow CO_2 + C$), which is favored at near ambient pressure conditions [1] and thus could not be observed in previous UHV experiments.
It has recently been shown [2] that the space between graphene layer and the substrate may act as a nano-reactor cavity where the activation barrier for CO oxidation is effectively reduced.
Exposing single layer graphene on Ni(111) to CO at 3.7 mbar, CO intercalates under the layer causing its detachment from the substrate. The so-obtained high local CO coverage under graphene cover enables the formation of CO_2 via the Boudouard reaction catalyzed by the Ni(111) surface already at 340 K [3]. The carbon produced by the reaction is used to transform residual carbide into graphene.
Moreover, under such conditions a chemisorbed CO species forms above the graphene film, thus paving the use of supported graphene for catalysis. The equilibrium coverage obtained under NAP conditions of this species at room temperature is compatible with the adsorption energy estimated in Ultra High vacuum experiments after exposure of graphene on Ni(111) to CO at liquid nitrogen temperature [4].
We also investigated the effect of the presence of vacancies obtained by low energy ion bombardment.
We find that CO intercalates at a rate which is comparable to the one observed in absence of defects and reacts via the Boudouard reaction producing additional carbon atoms and CO2.
While the former attach to the graphene layer and extend it over areas previously covered by carbide, the CO2 molecules bind to the graphene vacancies thus mending the defects. The so-formed complexes give rise to a peak at 533.4 eV which persists upon evacuating the vacuum chamber at room temperature and which we assign to a covalently bonded species containing C and O [5].
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