CO intercalation and Boudouard reaction under graphene cover on Ni(111)

G. Carraro[1], M. Smerieri[1], L. Savio[1], M. Lewandowski[2], M. Rocca[3,1] and L. Vattuone[3,1]

[1] *IMEM-CNR, UOS di Genova, 16146 Genova, Italy*
[2] *NanoBioMedical Centre, Adam Mickiewicz University, 61-614 Poznan, Poland*
[3] *DIFI, University of Genoa, 16146 Genoa, Italy*

giovanni.carraro@imem.cnr.it

Ni is a known catalyst for the Boudouard reaction (CO+CO → CO_2 + C) which is favored by high pressure, escaping, so far, direct investigation under operando conditions. We thus devised and performed Near Ambient Pressures XPS experiments at Tempo beamline of Soleil Synchrotron.

Our results show that graphene can be grown via a Boudouard reaction when exposing the bare Ni(111) to CO, but only in NAP conditions (P_{CO}∼2 mbar). The temperature required is as low as 550 K [1], significantly less than the one required to grow by carbon segregation from the bulk (670 K).

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.

We demonstrated that CO can effectively intercalate under the graphene cover on G/Ni(111) and that the so-obtained high local CO coverage enables the formation of CO2 via Boudouard reaction. The reaction takes place already at 340 K [3], which is, again, lower than the temperature required for the reaction on bare Ni(111)

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 found 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 CO_2 [5].

We acknowledge support by MIUR (projects PRIN2017 no. 2017NYPHN8 and 2017KFMJ8E_003) and by Fondazione Compagnia di S. Paolo (project MC-nano).

[1] R. Davì *et al.* Chem. Phys. Lett. **774**, 138596 (2021)
[2] Q. Fu and X. Bao, Chem. Soc. Rev. **46**, 1847 (2017)
[3] R. Davì *et al,* Appl. Surf. Sci. **599**, 154065 (2022)
[4] M. Smerieri *et al*, Chem Cat Chem **7**, 2328 (2015)
[5] R. Davì *et al*, Phys. Chem. Chem. Phys. **24**, 28486 (2022)