Intercalation of carbon monoxide in sub-monolayer graphene on Pt(001)

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Intercalation of molecules between metal substrates and graphene or other two-dimensional (2D) systems may find consistent applications in catalysis. In particular, the space between a metal surface and a 2D layer can be considered as a nanoreactor, where chemical reactions that do not take place on the bare metal surface may occur.

In this study we focused on CO intercalation in a 2D nanoreactor formed by weakly interacting graphene synthesized on Pt(001). The experiments were performed in an ultrahigh vacuum system, CoSMoS, which is a surface science cluster system connected to the SuperESCA beamline at the Elettra synchrotron radiation facility. Graphene (Gr) was produced *in situ* by chemical CVD by dosing ethylene at high temperature, following the evolution of the C 1s spectrum in real time with fast-XPS. The LEED pattern shows the presence of rotational domains on the surface but the C1s peak is very narrow due to a weak interaction between Gr and the Pt substrate. In order to intercalate CO it was necessary to dose less than a full Gr layer or to remove part of the layer with an oxygen treatment at high temperature. A number of techniques were used to characterize the electronic, structural and chemical properties of the system: HR-XPS, XPD, STM and NEXAFS. The results showed that after CO intercalation the C 1s peak of graphene shifts towards lower binding energies by 0.2 eV, indicating that Gr is decoupled from Pt(001). Also, the lineshape of the C1s core level of intercalated CO resembles that of CO/Pt(001), meaning that the CO molecules occupy the same adsorption sites with similar configuration in the two systems. Fast XPS measurements during sample heating demonstrate that the graphene cover confers an enhanced thermal stability to the CO adsorbed on Pt(001). Therefore Gr/Pt(001) appears to be a good candidate for tuning catalytic processes such as CO oxidation.

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