Inverse metal-oxide nanocatalysts are of paramount interest in the development of efficient catalytic materials.[1] In particular, ZnO nanofilms epitaxied on Pt(111) provide the opportunity to explore possible synergetic effects of the Pt/ZnO system regarding the oxidation of CO. Indeed kinetic studies suggest that partly dewetted ZnO(0001) films lying on Pt(111) single crystal are much more efficient to catalyse the CO oxidation reaction than the bare Pt surface itself. This effect is attributed to the specific chemistry of the Pt/ZnO boundaries. [2] The present study is in the wake of a recent work by our group where near-ambient X-ray photoemission spectroscopy (NAP-XPS) was used to monitor the catalytic oxidation of CO over ZnPt nanoparticles (NPs). [3,4] By using well characterized systems formed on single crystal surfaces, we aim at reducing some uncertainties on the morphology and chemistry encountered in the case of NPs, on the one hand, and at providing advanced surface chemistry insights (especially the molecular bonding) that were not addressed in [2], on the other hand.

To examine the surface chemistry of the ZnO/Pt(111) system, we used NAP-XPS operated under 1 mbar of O₂:CO mixture (4:1) at TEMPO Beamline SOLEIL, the French synchrotron source. The adsorption of the reactant molecules and the CO oxidation reaction itself were monitored in situ in a temperature range between room temperature and 450 K. Since NAP-XPS enables the collection of photoelectrons from both the gas and solid phases, we can relate the gas phase composition (reactants and products), with the chemical state of the surface Adsorbed CO was seen on bare Pt(111) at C 1s binding energies (BE) of 286.7 and 286.0 eV, occupying on-top and bridge sites, respectively (Fig. panel (a)). The ZnO nanofilm on Pt(111) appeared discontinuous as the C 1s components relative to CO adsorbed on bare Pt(111) patches coexisted with a carbonate signal (Fig. panel (b)). The latter one resulted from the oxidation and adsorption of CO on the ZnO patches. This view was corroborated by the STM image (Fig. panel (c)) of the starting surface where bare Pt patches amount to ~20% of the surface, the rest (80%) corresponding to 1 ML ZnO (moire) and 2 ML ZnO. Therefore, the conditions leading to a possible Pt/ZnO synergetic effect, according to [2] are met. The onset of CO oxidation reaction is observed at 380 K both for bare Pt(111) and ZnO/Pt(111) from the appearance of the CO₂ gas phase in the C 1s spectra at a BE of 292 eV (referenced to the Pt Fermi level). A detailed analysis of the calibrated intensities of carbonates, adsorbed CO and gas phases (CO and CO₂) was performed from C 1s, O 1s and Pt 4f spectra to monitor the surface chemistry as the CO₂ yield increases with increasing temperature. The issue of the synergetic effect provided by the Pt/ZnO combination will be discussed in detail, from a careful examination of the NAP-XPS spectra.

Figure: (a-b) In situ core-level spectra of the C 1s recorded at a photon energy hν = 400 eV. (c) 3D STM image (2.1 V, 0.5 nA) of a ZnO thin film (~1 ML thick) as deposited on Pt(111). CO_{(g)} is CO gas phase. CO_{(ad)} corresponds to adsorbed CO. CO₂(g) is the produced CO₂ gas phase. Carb* are carbonates species. C_{(gr)} is the graphitic carbon.

References: