CO adsorption on clean and oxidized $Pt_3Ti(111)$ studied by IRRAS and XPS

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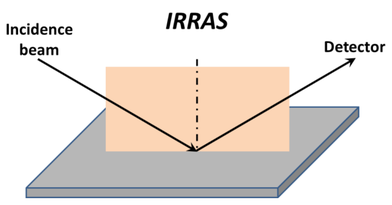
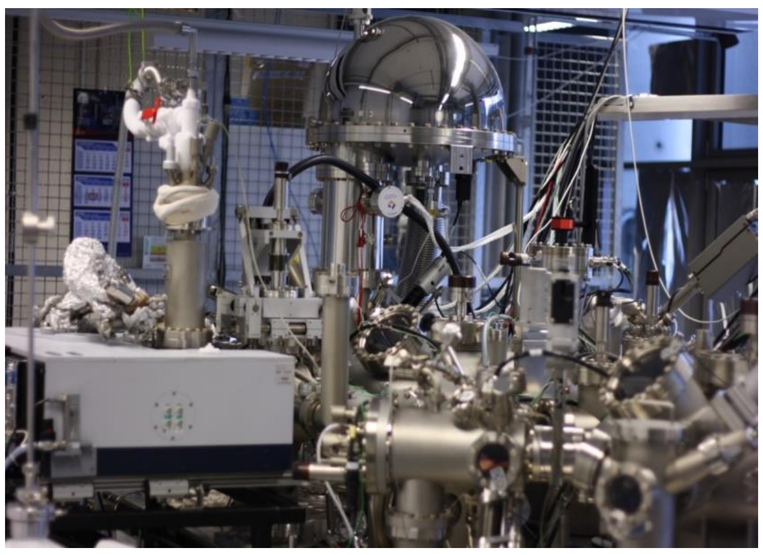
Introduction

The intermetallic alloy Pt_3Ti is a promising representative for titania (TiO_2) based catalysts. It is known that oxidation of $Pt_3Ti(111)$ under moderate preparation conditions leads to the formation of closed and well ordered ultrathin TiO_x films. The latter are expected to exhibit new structural and electronic properties that are quite different from the bulk TiO_2. In this work we present a surface science study of CO adsorption on pure and oxidized $Pt_3Ti(111)$ single-crystal surfaces by employing infrared reflection absorption spectroscopy (IRRAS) in combination with X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED).



UHV-IR/XPS apparatus "THEO"

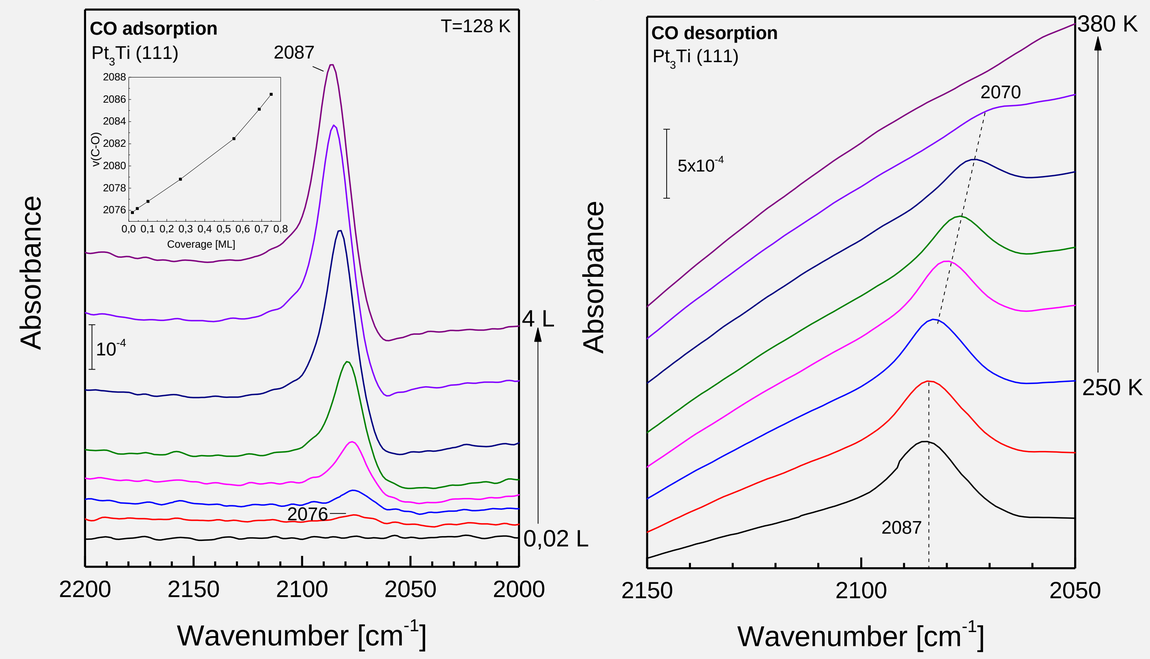


Experimental

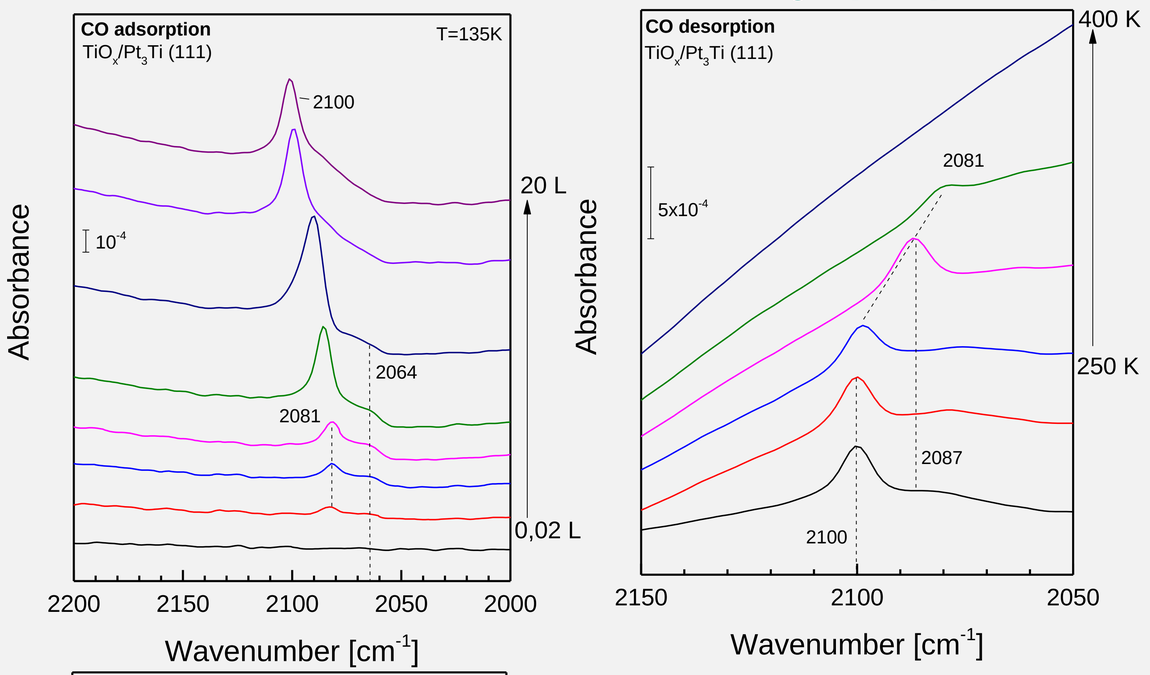
The series of measurement was carried out in our own UHV-chamber with a base pressure of 10^{-10} mbar. The Pt_3Ti (111) single crystal was mounted on a sampleholder with e-beam heating. The alloy crystal was cleaned by repeated cycles of sputtering with 3,0 kV Ar^+ ions at 900 K and subsequent annealing at 1100 K. For temperature displaying a K-type thermocouple was attached on the sample holder heating plate. After cooling carbon monoxide was dosed for several portions over a leak valve in the IR-compartment. At saturated coverage the temperature was elevated and spectra were recorded at a given set of temperatues for monitoring the CO desorption process. Ultrathin titanium oxide film growing was tested referring a literature known recipe at 1000 K for different oxygen dosages. XPS measurements were performed under grazing incidence conditions in order to resolve highly precise the appropiate surface composition.

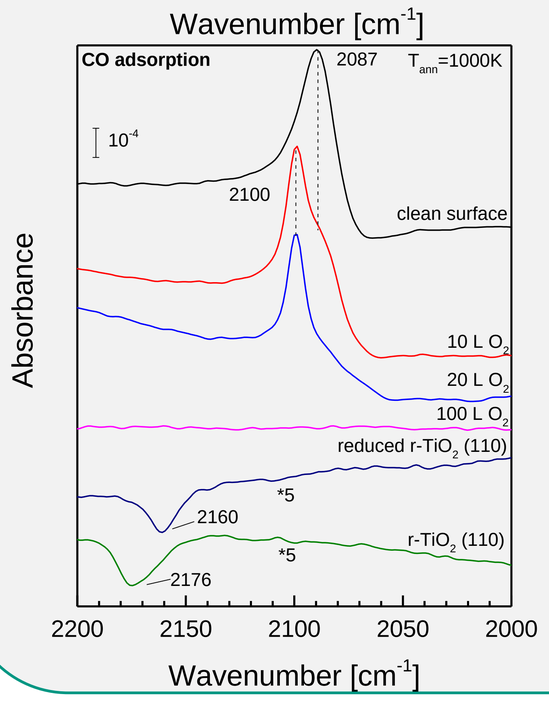
IRRAS experiments

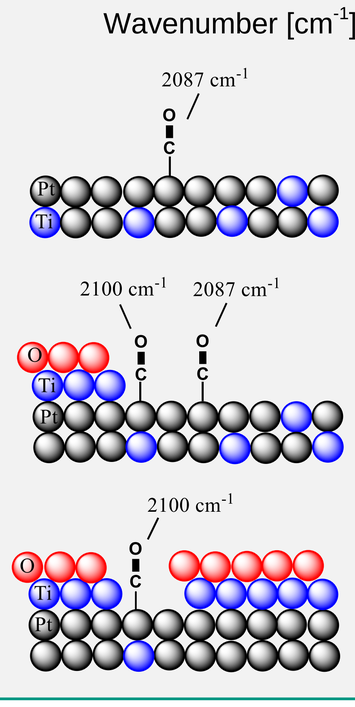
CO on $Pt_3Ti(111)$



CO on low oxidized $Pt_3Ti(111)$

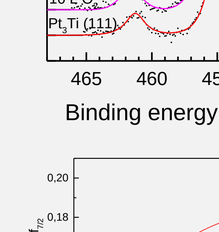
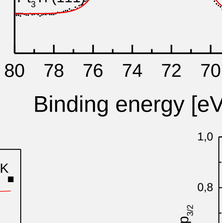
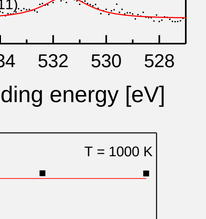






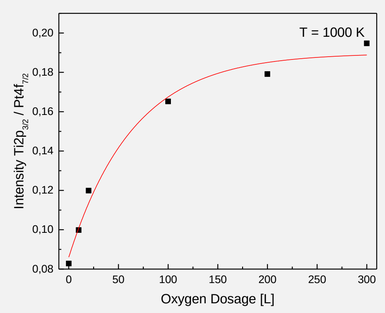
LEED

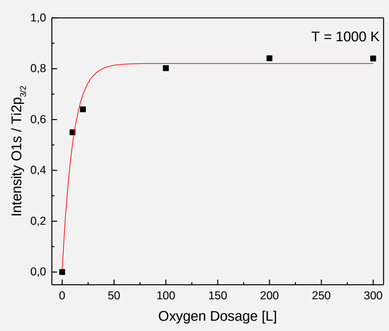
Structure of pure and oxidized $Pt_3Ti(111)$ surfaces

Pt_3Ti (111)	Pt_3Ti (111) + 200 L O_2 at 1000 K	Pt_3Ti (111) + 500 L O_2 at 1000 K
		
79 eV p (2x2)	80 eV z'-phase	80 eV w'-phase

XPS measurements

Peak evolution during oxidation of $Pt_3Ti(111)$ at 1000 K





Conclusions

- The pure $Pt_3Ti(111)$ is primarily Pt-terminated with a p(2x2) superstructure.
- CO adsorbs terminally (on-top) at Pt sites on pure $Pt_3Ti(111)$. A coverage-dependent blue-shift of the CO band (from 2176 to 2187 cm^{-1}) was observed, which is attributed to the lateral adsorbate-adsorbate interaction including dipole-dipole coupling and chemical shift.
- Oxidation of $Pt_3Ti(111)$ at 1000 K: a second CO band was observed at 2100 cm^{-1} which is assinged to CO adsorbed on Pt with adjacent TiOx thin films
- Expose of 100 L O_2 at 1000 K leads to the formation of a closed TiO bilayer which is O-terminated and shows an ordered hexagonal (7x7)R21.8° superstructure (w'-TiO phase).

References

1. S. Le Moal, M. Moors, J. M. Essen, C. Becker, K. Wandelt, *Surf. Sci.* **2010**, 604, 1637.
2. S. Le Moal, M. Moors, J. M. Essen. C. Breinlich, C. Becker, K. Wandelt. *J. Phys. Condens.* Matt. **2013,** 25, 11.
3. V. Schott, H. Oberhofer, A. Birkner, M. Xu, Y. Wang, M. Muhler, K. Reuter, C. Wöll, *Angew. Chem.* **2013**, 52, 11925.
4. F. Sedona, G. A. Rizzi, S. Agnoli, F. X. Llabres i Xamena, A. Papageorgiou, D. Ostermann, M. Sambi, P. Finetti, K. Schierbaum, G. Granozzi, *J. Phys. Chem. B* **2005**, 109, 2411.
5. J. Paul, S. D. Cameron, D. J. Dwyer, F. M. Hoffmann, *Surf. Sci.* **1986**, 177, 121.
6. W. Chen, S. Cameron, M. Göthelid, M. Hammar, J. Paul, *J. Phys. Chem.* **1995**, 99, 12892.