Probing the surface structure of thin TiO_x films on $Pt_3Ti(111)$ by IRRAS and XPS

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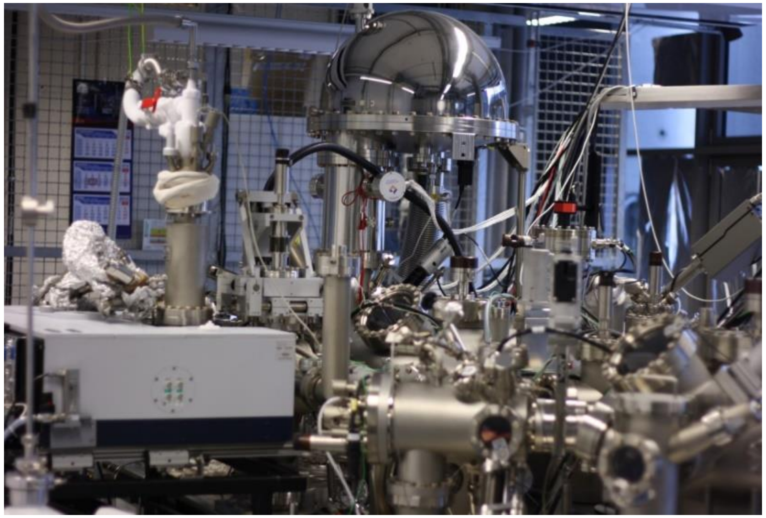
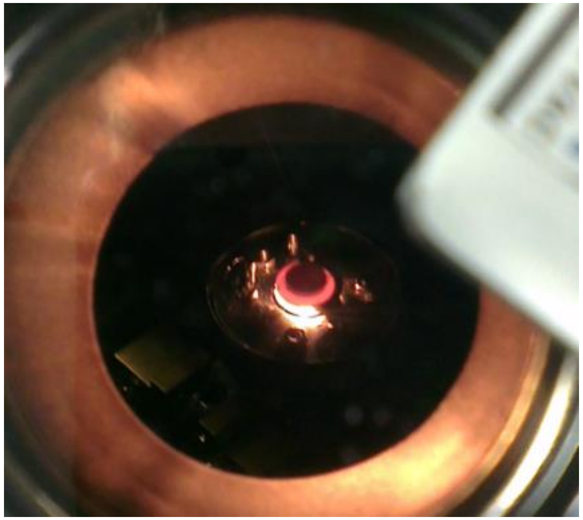
DPG meeting, Dresden, 21.03.2017

Institute of functional interfaces (IFG), Helmholtz-Research-School „Energy related catalysis“





Outline

Ⅰ Introduction

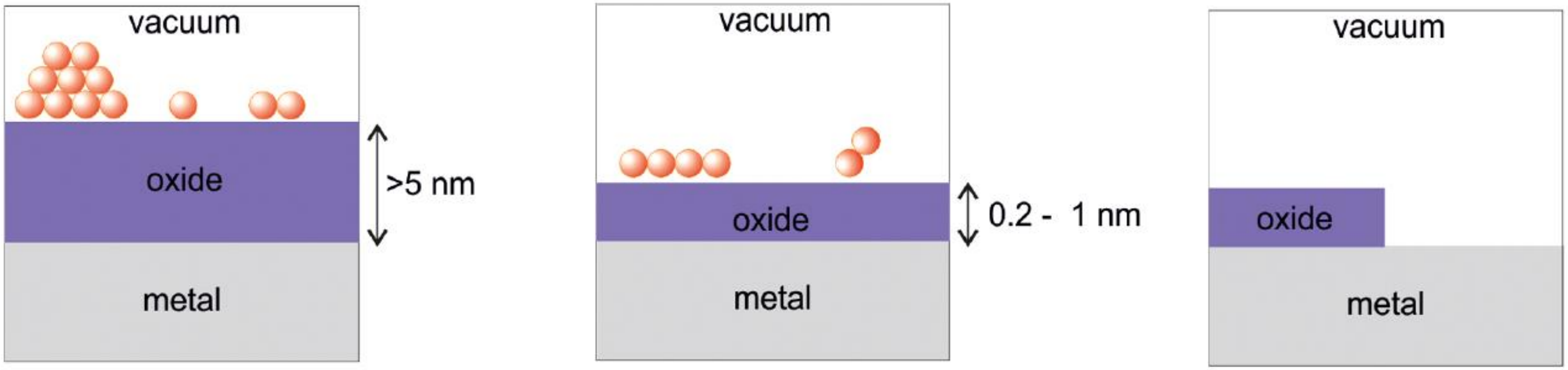
Ⅱ Experimental

Ⅲ Results and Discussion

Ⅳ Conclusions

I Oxide films as templates for catalysts

- Oxide films exhibit other structural and electronical properties than bulk oxide materials -> metal deposits agglomerate in different manner
- Challenge for catalyst modification: Tailoring Selectivity and Reactivity
- Physical background often referred with so called strong-metal support interactions (SMSI)
- Oxide films on metallic substrates are attractive candidates for surface science studies which bypasses the problem of charging effects

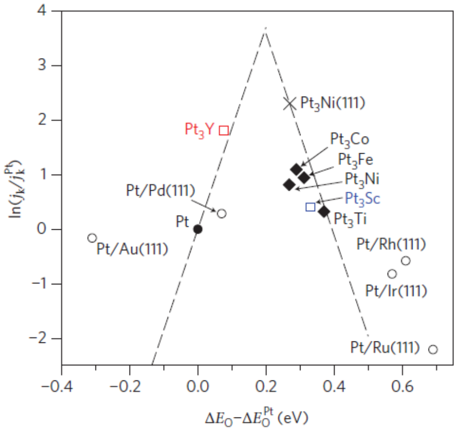


Different stereotypes of oxide films

H.-J. Freund, J. Am. Chem. Soc. 2016, 138, 8985-8996.

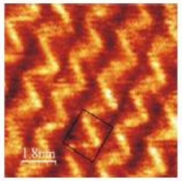
I Motivation for investigations on $Pt_3Ti(111)$

- Electrocatalysis: Electronical structure tuning on Pt-cathodes by auxillary ingredients may lead to improved activites for oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells (PEMFC)
- The (111) facet of Pt possess the lowest surface energy, ORR reactive
- Pt-Ti alloy crystal allows the facile generation of thin film structures and avoids the usage of atomic beam epitaxy from titanium vapor material on platinum
- Certain titanium oxide phases of distinctive morphology and stoichiometry can be synthesized on $Pt_3Ti(111)$ under defined preparation conditions in high reproducibility

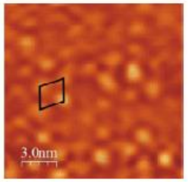


„Sabatier“ volcano

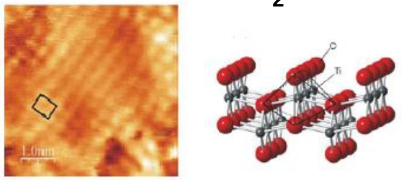
z‘-TiO_2



w‘-TiO_2

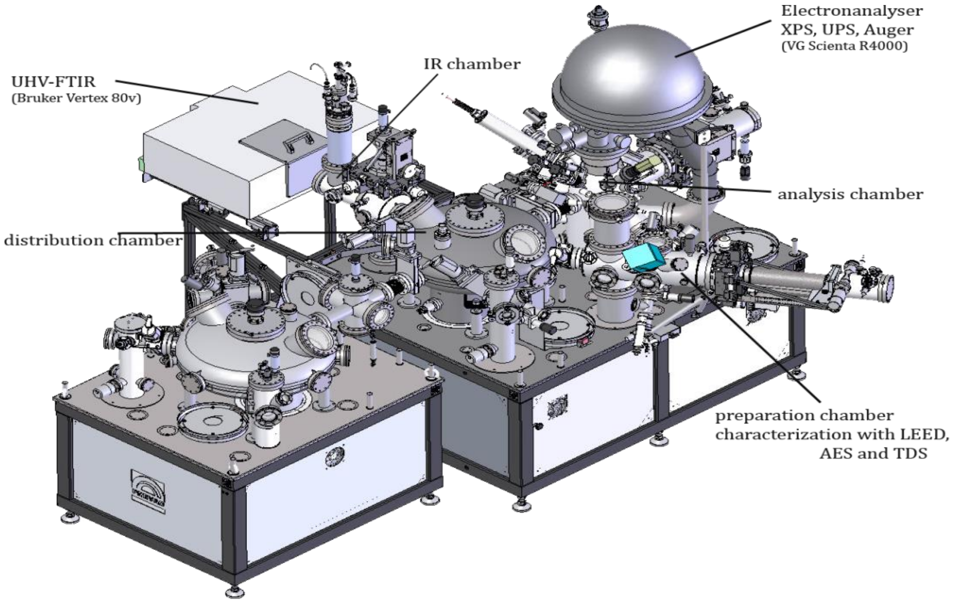


Rect-TiO_2



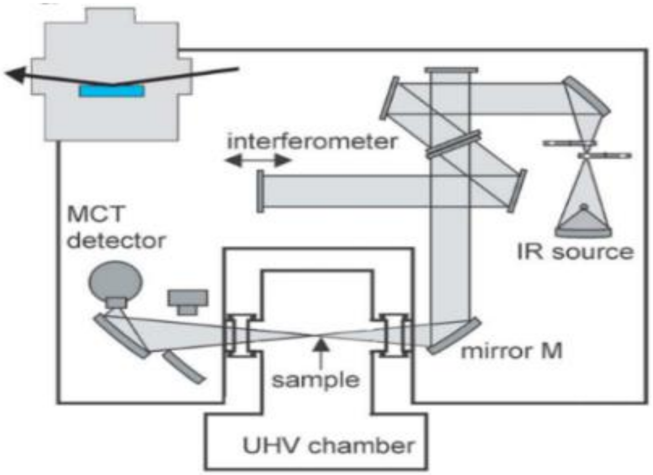
S.Le Moal, M. Moors, J. Essen, C. Breinlich, C. Becker, K. Wandelt, *J. Phys. Condens. Mat*. **2013**, 25, 4, 1-11.
J. Greeley, I. Stephens, A. Bondarenko, T. Johansson, H. Hansen, T. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. Norskov, *Nat. Chem* **2009**, 1, 552–556.
C. Breinlich, M. Buchholz, M. Moors, S. Le Moal, C. Becker, K. Wandelt, *J. Phys. Chem. C* **2014**, 118, 6186-6192.

Ⅱ UHV-apparatus „THEO“



Basic concept and capacities

- UHV enables adsorption measurements on the low reflective class of metaloxides with a common FT-IR-spectrometer
- Equipped with XPS, LEED, IR, AES, UPS, TDS
- Sample heating up to 1200 K
- Ingenious sample transfer system



IR features

- IR-Reflectance absorbance mode for single crystals in grazing incidence (θ=80°)
- IR-Transmission mode for powder samples
- Sample cooling to 100 K (LN_2) or 60 K (LHe) in IR chamber
- Integrated polarizer for s- and p- IR beams allows orientational studies of molecules deposited on surfaces

Ⅱ Strategies and advantages

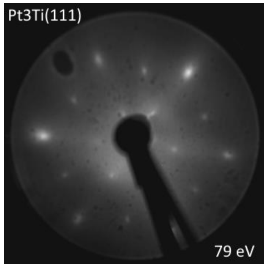
- Spectroscopical analysis as powerful and versatile tool for oxidation monitoring
- Not concerned and limited to crystallographic states
- CO molecule as probing agent for surface structure changes
- Both methods, IRRAS and XPS, can be combined for complementary studies

⇒ Investigations on initial stages seems legit

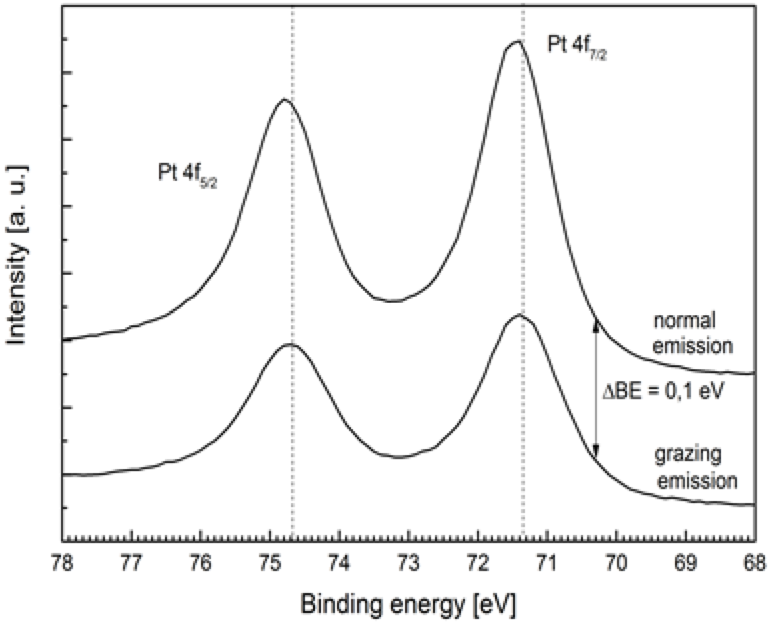
.

Ⅲ Preparation and termination of $Pt_3Ti(111)$

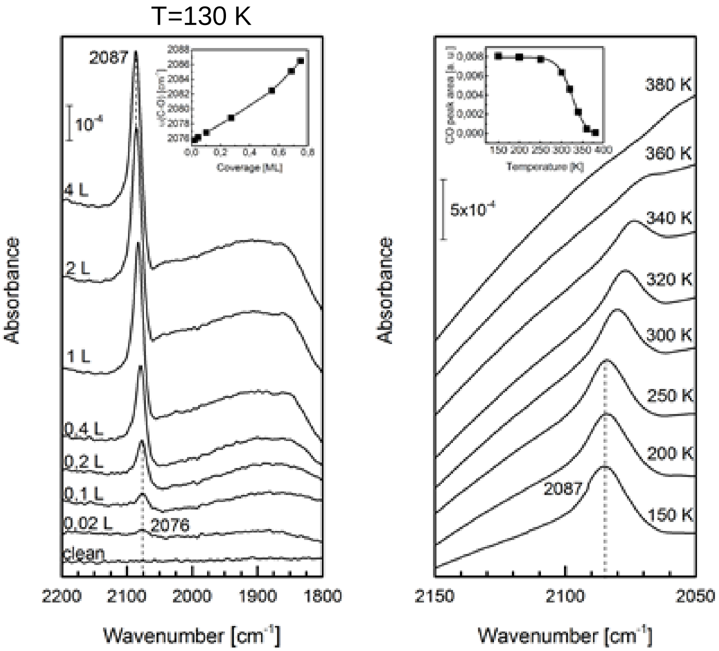
- Executed sample preparation: 3 kV Ar^+ sputtering energy 10 minutes, 1100 K annealing 15 minutes.
- CO probing by IRRAS may confirm defective surface structure for Pt-Pt_3Ti as recently reported.



LEED pattern p(2x2)



XPS spectra of Pt 4 core level of clean $Pt_3Ti(111)$ for grazing and normal emission



IRRAS: CO on Pt_3Ti

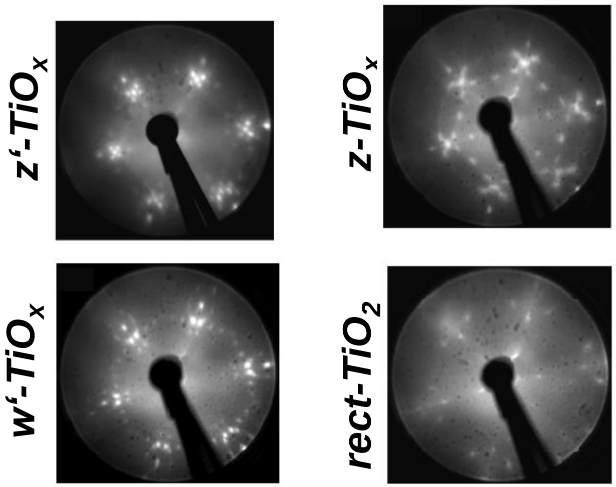
M. Paßens, V. Caciuc, N. Atodiresei, M. Moors, S. Blügel, R. Waser, S. Karthäuser, *Nanoscale* **2016**, 8, 13924-13933.
Severine Le Moal, M. Moors, J. M. Essen, C. Becker, K. Wandelt, *Surf. Sci*. **2010**, 604, 1637-1644.

Ⅲ Preparation of ordered oxide phases grown on $Pt_3Ti(111)$

- Oxidation between 500-800 K leads to the formation of disordered films
- Ordered oxide phases can be gained between 800-1100 K in dependency of oxygen dosages for partial pressures in $p(O_2)=10^{-8}-10^{-5}$ mbar range
- z‘-TiO_x (zig-zig-structure) and w‘-TiO_x (wagon-wheel) are temperature resistant phases, while incommensurate z-TiO_x and rect-TiO_2 structures comply metastable criteria as they will be transformed into w‘-TiO_x after a harsh postannealing treatment

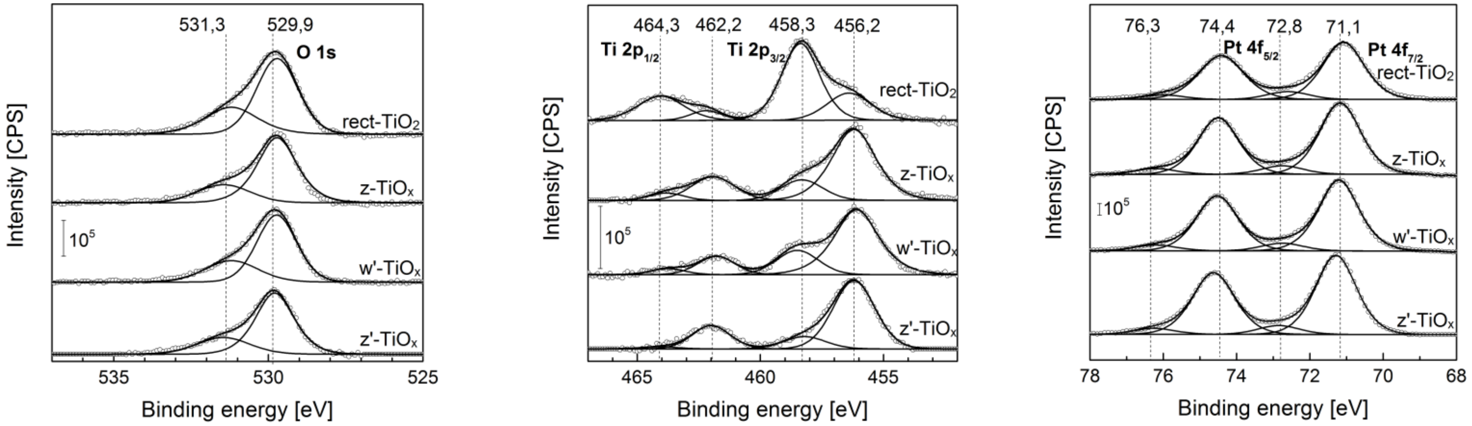
Oxide-phase	Synthesis	LEED
z‘-TiO_x	T = 1000 K 150-200 L O_2 10^{-8} mbar	6x3√3
w‘-TiO_x	T = 1000 K 500-4000 L O_2 10^{-7} mbar	(7x7)R21.8°
z-TiO_x	T = 800 K 900 L O_2 10^{-6} mbar	incommensurate
rect-TiO_2	T = 800 K 4500 L O_2 10^{-5} mbar	incommensurate

S.Le Moal, M. Moors, J. Essen, C. Breinlich, C. Becker, K. Wandelt, *J. Phys. Condens. Mat*. **2013**, 25, 4, 1-11.



Experimental phase diagram for O_2/Pt_3Ti and recorded LEED patterns of obtained oxide superstructures:

Ⅲ XPS studies on ordered $TiO_x/Pt_3Ti(111)$ films



Layer thickness

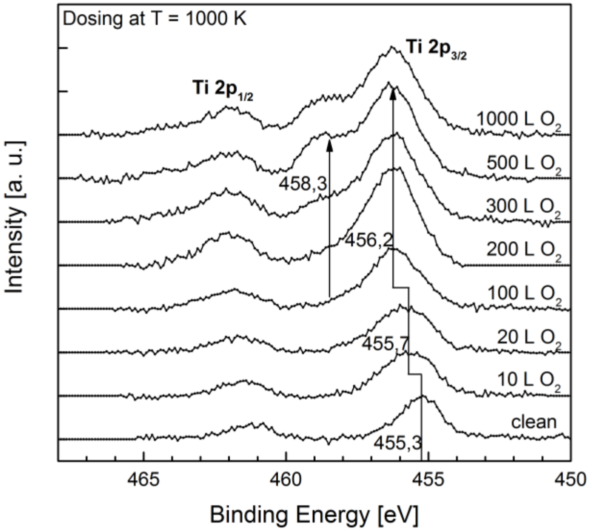
$$\frac{I_A}{I_S} = \frac{T_A \sigma_A n_A \lambda_{A,A}}{T_S \sigma_S n_S \lambda_{S,S}} \cdot \frac{1 - e^{-\frac{d}{\lambda_{A,A} \cos(\theta)}}}{e^{-\frac{d}{\lambda_{A,S} \cos(\theta)}}}$$

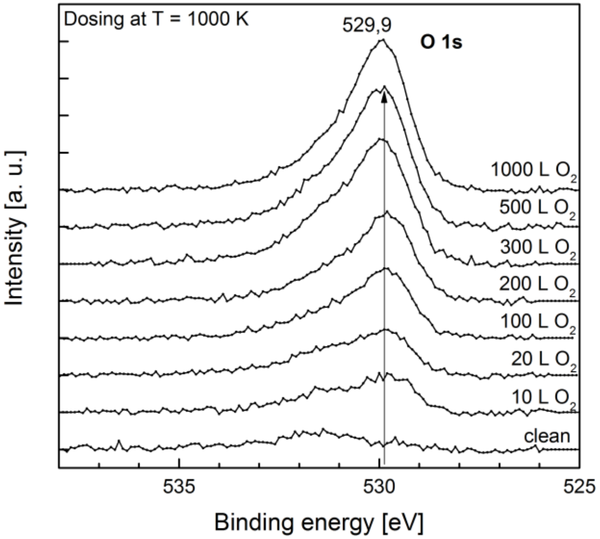
z‘-TiO_x:1,7 Å
w‘-TiO_x: 2,0 Å
rect-TiO_2: 2,6 Å

Species	Material	Binding energy [eV] This work	Binding energy [eV] Reference
Ti^{4+}	$TiO_x/Pt_3Ti(111)$	458,3	458,0
	$TiO_x/Pt(111)$		458,4
	TiO_2(bulk)		459,0
Ti^{3+}	$TiO_x/Pt_3Ti(111)$	456,2	456,3
	$TiO_x/Pt(111)$		456,2
	Ti_2O_3 (bulk)		457,5
Pt^{2+}	$Pt_3Ti(111)$	73,0	
	Pt Ti Powder		72,6
	$TiO_x/Pt_3Ti(111)$	72,8	
	Pt/CeO_2powder		72,8
Pt	$Pt_3Ti(111)$	71,3	71,5
	PtTi Powder		71,4
	Pt(111)		70,9
	$TiO_x/Pt_3Ti(111)$	71,1	
	Pt/CeO_2 powder		71,1

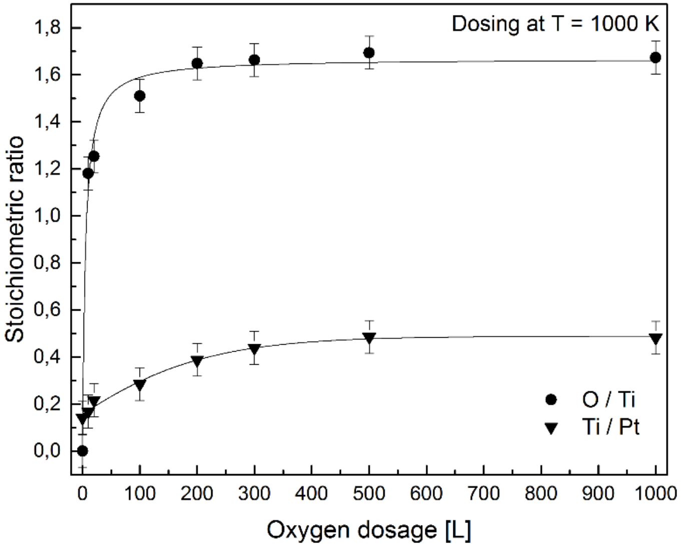
Oxygen on Pt(111) see ref. D. Fantauzzi, S. K. Calderon, J. E. Mueller, M. Grabau, C. Papp, H.-P. Steinrück, T. P. Senftle, A. C. T. van Duin, T. Jacob, *Angew. Chem*, **2017**, 129, 2638-2642. **Quantitative XPS see ref.** P. Streubel, R. Hesse, L. Makhova, J. Schindelka, R. Denecke, *Technical report* **2011**.

Ⅲ XPS: Effect of oxygen dosage on thin TiO_x film growth





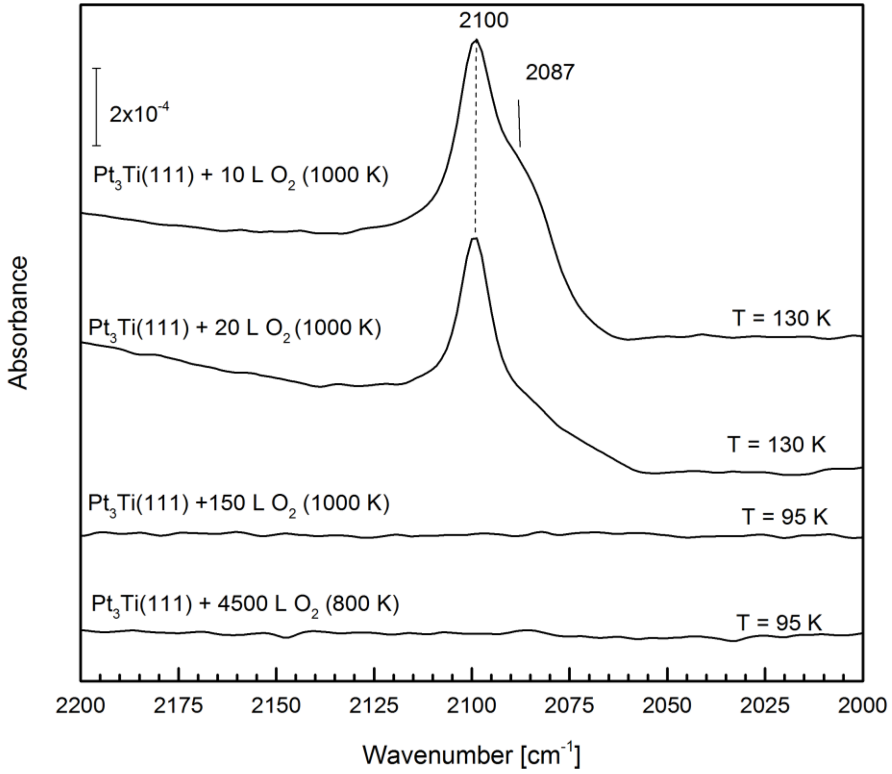
Ti_nO_{2n-1}	(2n-1)/n
TiO	1.0000
Ti_2O_3	1.5000
Ti_3O_5	1.6667
Ti_4O_7	1.7500
Ti_5O_9	1.8000
Ti_6O_{11}	1.8333
Ti_7O_{13}	1.8571
Ti_8O_{15}	1.8750
Ti_9O_{17}	1.8889
$Ti_{10}O_{19}$	1.9000
TiO_2	2.0000



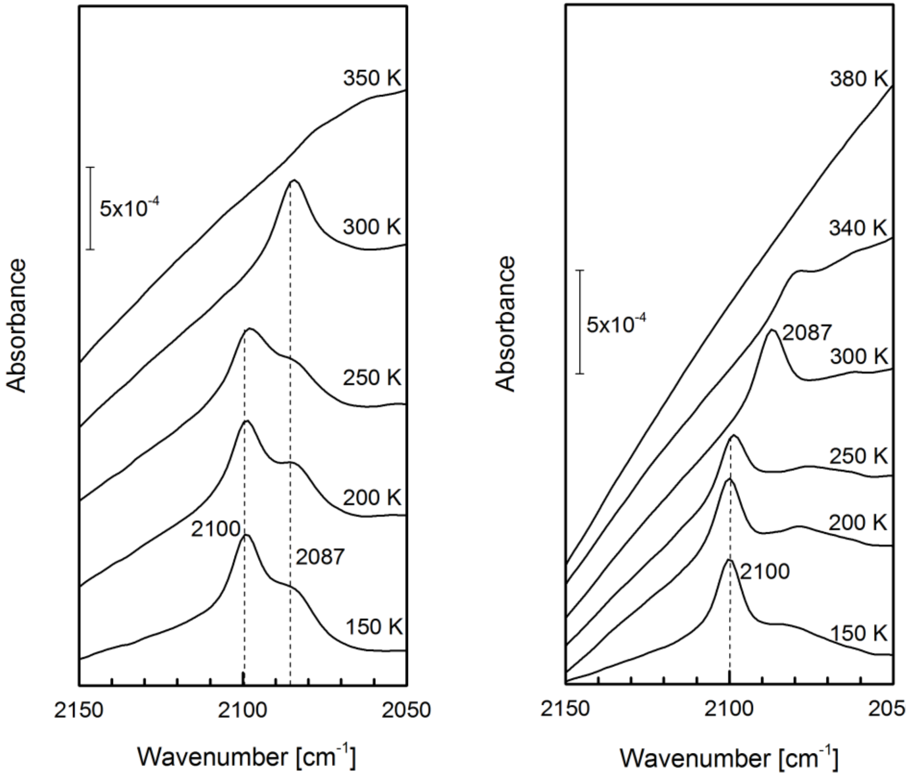
TiO: -123,9 kcal/mol
TiO_2: -224,9 kcal/mol
Ti_2O_3: -363,0 kcal/mol
Ti_3O_5: -586,7 kcal/mol
PtO: -17,0 kcal/mol
PtO_2: -32,0 kcal/mol

Ⅲ IRRAS on oxidized Pt$_3$Ti(111)

CO adsorption



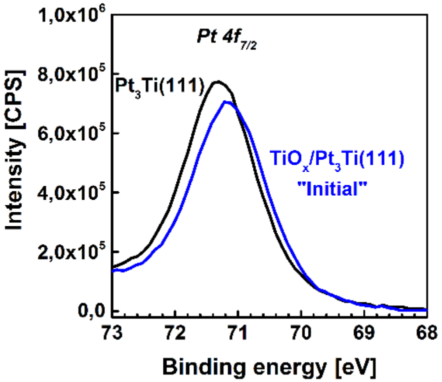
Heating experiment

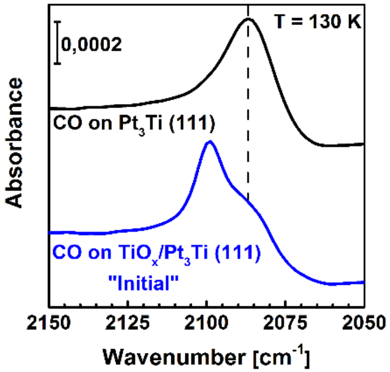


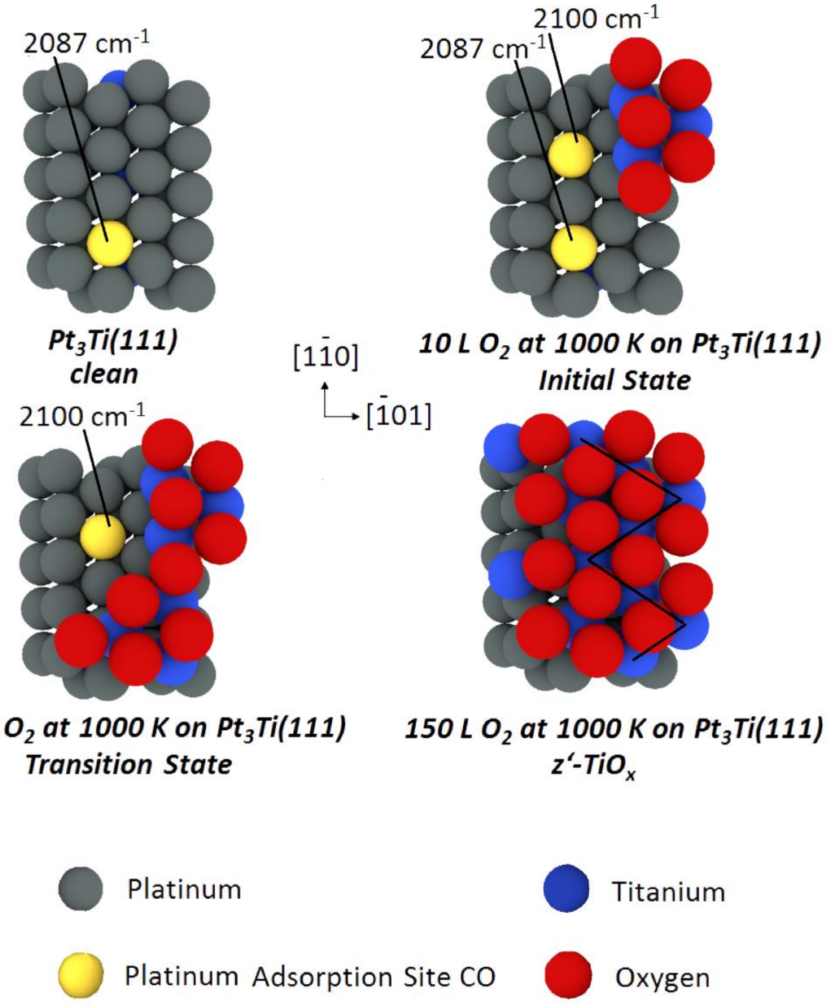
Pt$_3$Ti(111) + 10 L O$_2$
(1000 K)

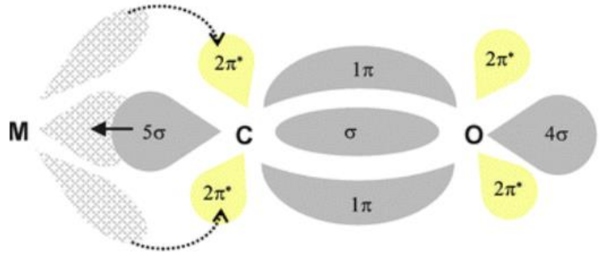
Pt$_3$Ti(111) + 20 L O$_2$
(1000 K)

Ⅲ Discussion









CO on Pt (Blyholder-model)
5σ CO => 6sp Pt
2π* CO <= 5d Pt

„2087 cm^{-1} "Pt d-band narrowed by subsurface titanium

„2100" cm^{-1} in agreement with Pt(111)
$Pt_3Ti(111)+O_2$ -> $TiO_x/Pt(111)$

Ⅳ Conclusion

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- All common oxide overstructures exist in mixtures of Ti^{3+}/Ti^{4+} and close the surface in oxygen termination
- Layer thickness calculations let us assume a O-Ti bilayer stacking for z‘ and w‘, but a O-Ti-O trilayer film for rect-TiO_2 on a platinum terminated interface
- For low oxidized $Pt_3Ti(111)$ (O_2 dosage < 20 L) Ti^{2+} was proposed as intermediate species
- IRRAS data for CO on clean Pt_3Ti (111) reveal the complex surface structure for alloyed materials including Pt d-band narrowing by Ti-doping
- CO adsorption behavior on $Pt_3Ti(111)$ quite similar to Pt(111)
- Surface segregation of titanium during oxidation of $Pt_3Ti(111)$ confirmed by CO stretch vibration blueshift from 2087 cm^{-1} to 2100 cm^{-1}
- CO induced surface reduction of low oxidized $Pt_3Ti(111)$ properly observed near desorption temperature

Thank you for your attention!