Introduction

- Ru poor catalyst for CO oxidation at low pressure conditions, good at high pressure [1]
- When Ru surfaces are exposed to large amount of O_2 surface oxides (RuO_2) are formed [2]
- Oxidation of Ru(0001) leads to epitaxial formation of domains of RuO_2(110) in addition to regions of Ru(0001)-(1×1)-O (FIGURE 1) [3]

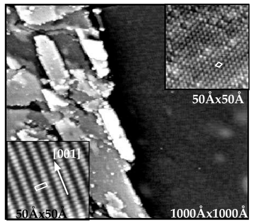

FIGURE 1

- Experiments with LEED, STM, ...
- Here: DFT-GGA calculations

Bulk RuO_2

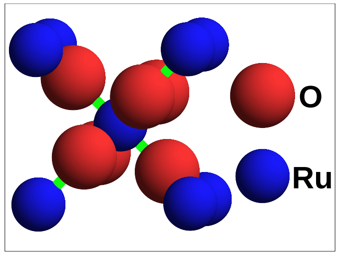

FIGURE 2

- Only one crystalline oxide of Ru known
- Bulk structure: Rutile (FIGURE 2)
- A <u>metallic</u> oxide
- Oxygen 3-fold, ruthenium 6-fold coordinated in the bulk
- RuO_3, RuO_4 volatile, poisoneous
- $a = 4.656$ Å, $c/a = 0.6940$ DFT-GGA
- $a = 4.511$ Å, $c/a = 0.6894$ expr

Clean RuO_2(110)

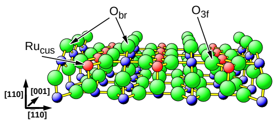

FIGURE 3

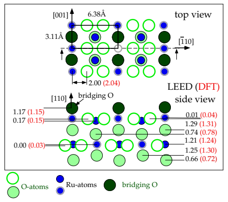

FIGURE 4

- The clean surface is stoichiometric and autocompensated (FIGURE 3), similar to TiO_2(110)
- E_{surf} = 70.7 meV/Å^2
- ϕ = 5.8 eV
- Experimental and DFT-GGA geometries agree excellently (FIGURE 4)
- All but two atoms in the surface unit cell are fully coordinated:
  - O_{br}: 2-fold coordinated, strongly bound ("water")
  - Ru_{cus}: 5-fold, coordinatively unsaturated site [4]

Coordinatively unsaturated site (CUS)

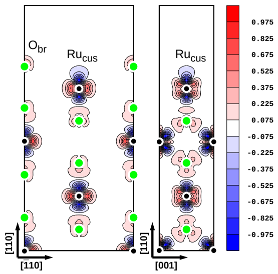

FIGURE 5

- $\Delta n(\mathbf{r}) = n_{\mathrm{RuO_2}}(\mathbf{r}) - \sum_I n_{\mathrm{atomic}}(\mathbf{R}_I)$
- Red regions = electron depletion, blue = accumulation
- The density difference at the 5-fold coordinated Ru_{cus} atom is like a continuation of the bulk, *<u>not</u>* screened like expected on a metallic surface
- ⇒ A directional "lone pair" pointing out from the surface

CO/RuO_2(110)

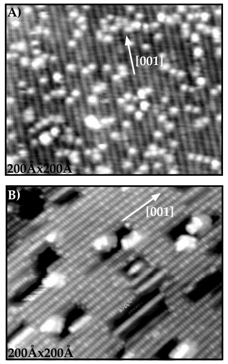

FIGURE 6

- CO molecules adsorb in the strands between the oxygen rows (FIGURE 6A)
- Similar 1-fold coordination as on Ru(0001) (FIGURE 7)
- 5σ-like orbitals become partially emptied, $2\pi^*$-like orbitals somewhat occupied (FIGURE 8)
- ⇒ The Blyholder model [5] is qualitatively applicable to CO/RuO_2(110)
- The diffusion barrier is 1 eV, much larger than on Ru(0001), so that at room temperature the molecules are immobile

CO/RuO_2(110)

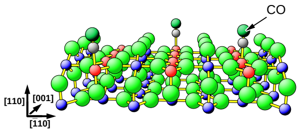

FIGURE 7

Large adsorption energies (eV):

	Ru(0001)	RuO_2(110)
CO	1.8	1.2
N_2	0.59	0.55

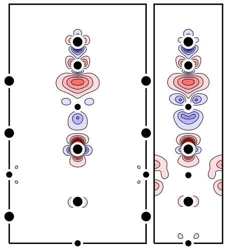

FIGURE 8

N_2/RuO_2(110)

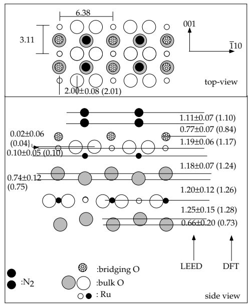

FIGURE 9

- N_2 is iso-electronic with CO
- N_2 molecules chemisorb above cus-Ru atoms similar to CO (FIGURE 9)
- This behaviour can be exploited to block the cus-Ru atoms selectively and hence to study the activity of cus-Ru atoms

Conclusions

- Ru(0001) oxidises forming domains of clean RuO_2(110)
- Ru_{cus} shows strong bonding characteristics, is an reactive site
- CO adsorbs according to Blyholder model
- Oxygen is bound weaker than on Ru(0001), CO still strongly
- ⇒ Preferable conditions for CO oxidation

References

[1] H-I Lee & J M White, J Catal **63** (1980) 261; N W Cant, P C Hicks, B S Lennon, J Catal **54** (1978) 372; C H F Peden in *Surface Science of Catalysis*, ACS Symposium Series 483 (1992) 143

[2] A Böttcher, H Niehus, S Schwegmann, H Over & G Ertl, J Phys Chem **101** (1998) 11 185; A Böttcher, M Rogazia, H Niehus, H Over & G Ertl, J Phys Chem **103** (1999) 6267

[3] H Over, Y D Kim, A P Seitsonen, S Wendt, E Lundgren, M Schmid, P Varga, A Morgante & G Ertl, Science **287** (2000) 1474

[4] R L Burwell, G L Haller, K C Taylor & J F Read, Adv Catal **20** (1969) 1

[5] G Blyholder, J Phys Chem **68** (1964) 2772

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STUDIES ON OXIDISED RUTHENIUM SURFACES

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