

ZERNIKE INSTITUTE COLLOQUIUM

Thursday, April 5th, 2018

16:00h, Lecture Hall: 5111.0080

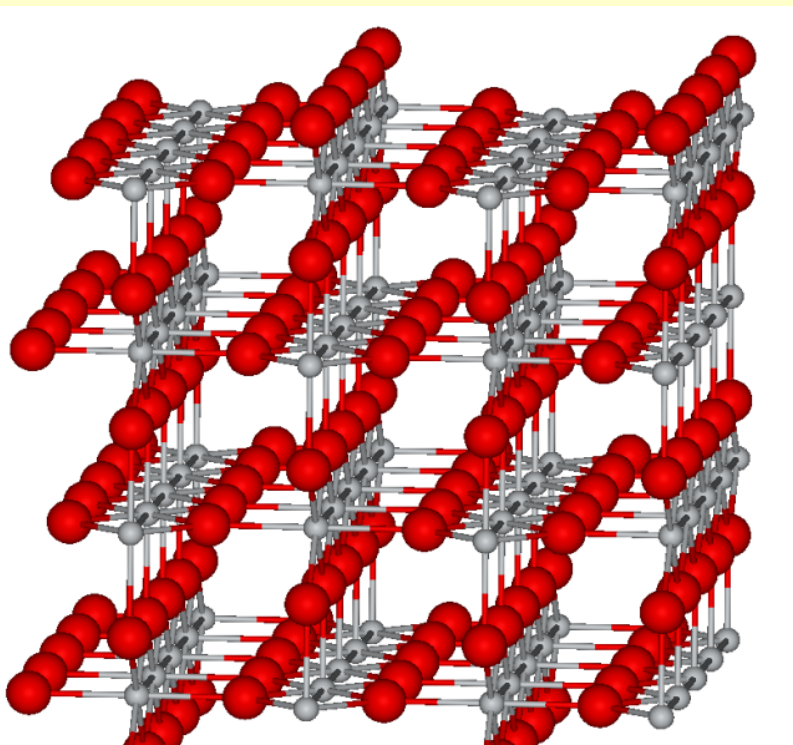
Coffee and cakes from 15:30h

Titania

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The future sustainable production of chemicals will stem on catalysts minimising the energy required for bond breaking and bond making. However, actual heterogeneous catalysts need rare and costly metal cocatalysts. But how should a catalyst look like to be efficient, cheap, earth abundant and non toxic? Ideally it should use renewable energies for the extra energy still needed in the processes. Such a hot candidate is titania which already is used for detoxification of waste water from organic molecules using solar energy and as heterogeneous catalyst for a number of other reactions. The literature on titania is vast and very often contradictory. I shall show that the reason for this is that the type of reaction products obtained is strongly dependent on the number of defects not only present at the surface but also in the bulk of titania. We have particularly studied the principle interactions of various oxygen containing organic molecules also in coadsorption with molecular oxygen and oxygen adatoms by means of surface science techniques.



Beside oxygen vacancies titania may contain Ti^{3+} interstitials which can lead to self doping of bulk TiO_2 even in high concentrations [1]. Above 410 K these defects start to diffuse towards the surface and may act as reaction centers. Thus titania may consist of Ti(III)/Ti(IV) redox pairs with scalable concentrations which can be activated via the proper temperature choice. Adsorption of oxygen leads to the formation of $\text{O}_2^{\delta-}$ or $\text{O}_{\text{ad}}^{\delta-}$ -atoms depending on the Ti^{3+} density. The activated oxygen reacts to form TiO_2 -islands at temperatures above 360 K with Ti^{3+} in close neighborhood to the surface and above 410 K with deeper defects diffusing towards the surface [2]. The strong affinity with respect to oxygen is the key for titania activated reactions of oxygen containing organic molecules [3]. Depending on the molecular

structure of the reacting species, particularly the absence or presence of α -CH-atoms in the vicinity of the oxygen containing group, C-C-coupling or partial oxidation reactions may be observed depending on coadsorbed activated oxygen and the bulk defect density. Surface science studies at rutile- $\text{TiO}_2(110)$ with model reactions of methanol, benzaldehyde and acetone will be presented [4].

[1] M. Li, W. Hebenstreit, U. Diebold, A. M. Tyryshkin, M. K. Bowman, G. G. Dunham, M. Henderson, *J. Phys. Chem. B*, **2000**, *104*, 4944-4950.

[2] M. A. Henderson, W. S. Epling, C. L. Perkins, Ch. H. F. Peden, U. Diebold, *J. Phys. Chem. B*, **1999**, *103*, 5328-5337; E. Lira, J. Ø. Hansen, P. Huo, R. Bechstein, P. Galliker, E. Lægsgaard, B. Hammer, St. Wendt, F. Besenbacher, *Surface Science*, **2010**, *604*, 1945-1960.

[3] U. Diebold, *Surf. Sci. Reports*, **2003**, *48*, 53-229.

[4] P. M. Clavin, C. M. Friend, K. Al-Shamery, *Chem. Eur. J.* **2014**, *20*, 7665-7669.



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