The Abdus Salam International Centre for Theoretical Physics

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2145-27

Spring College on Computational Nanoscience

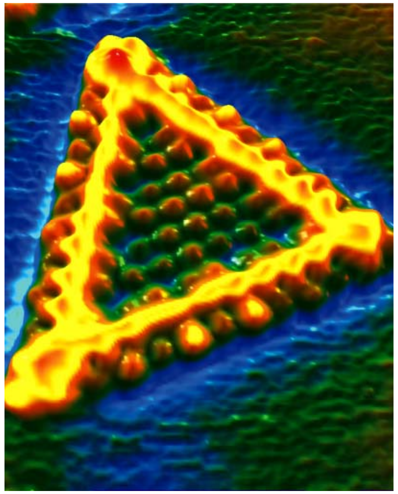
17 - 28 May 2010

Dynamics of Nanoclusters on Nanoclusters on Surfaces studied by Fast Scanning STM (Catalytical Model Systems studied by High Resolution, Fast-scanning STM)

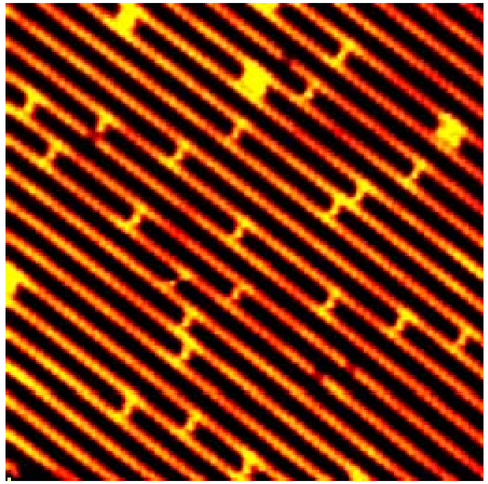
Flemming BESENBACHER
iNANO Interdisciplinary Nanoscience Center
University of Aarhus
Denmark

Spring College on Computational Nanoscience,Trieste May 2010

Catalytical model systems studied by high resolution, fast-scanning STM



Flemming Besenbacher
Email: fbe@inano.au.dk



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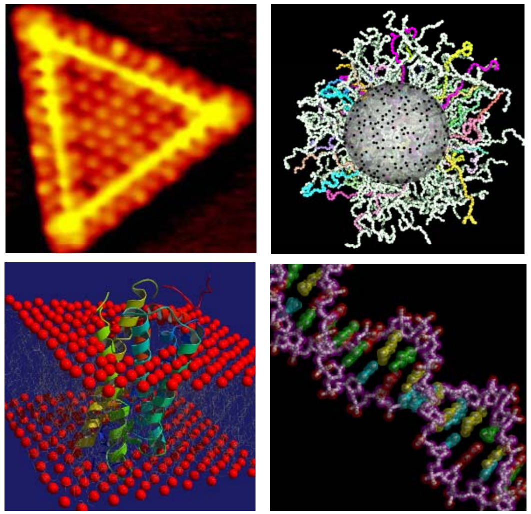

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www.inanoschool.au.dk

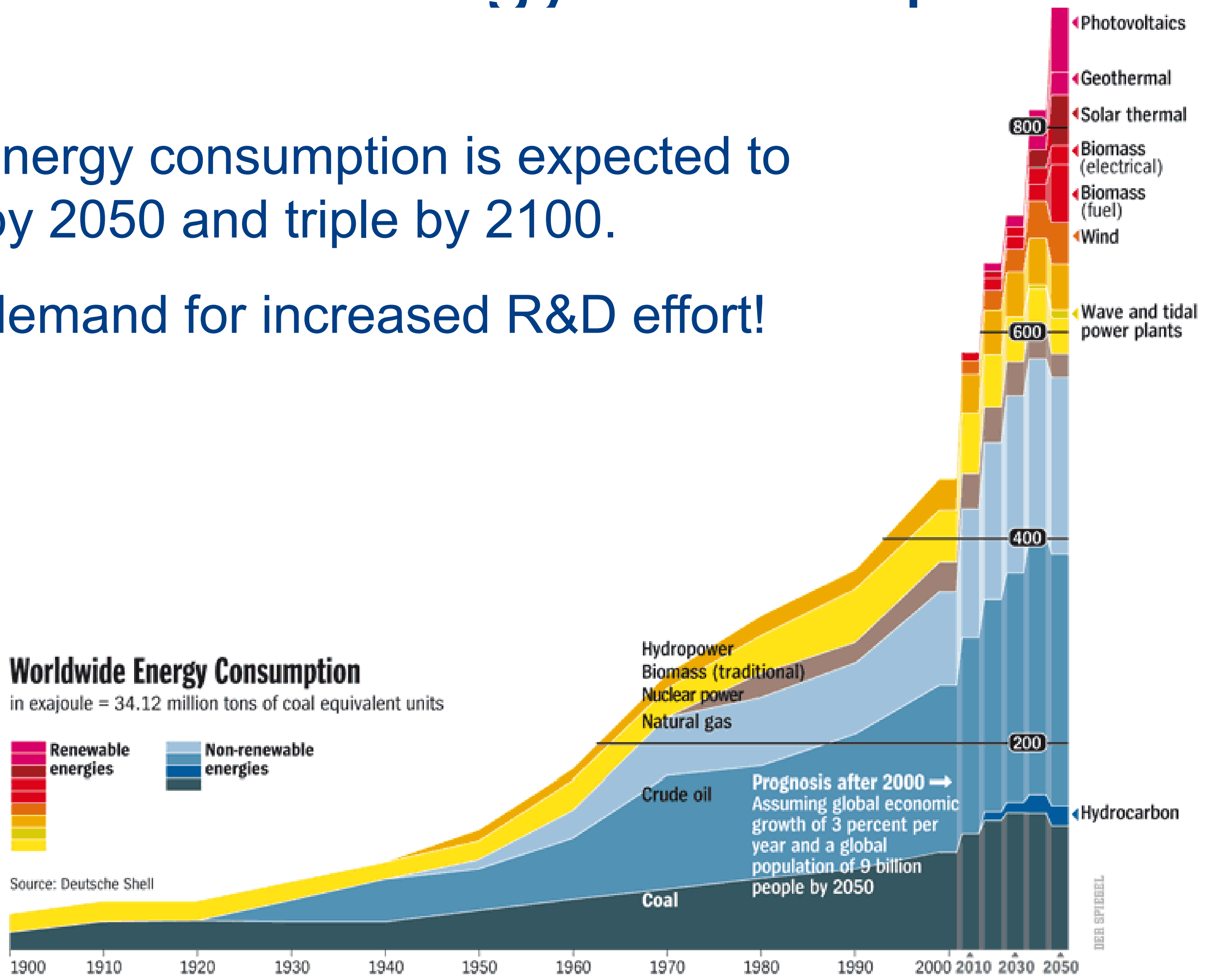
21st Century Challenges
Scientific Social Responsibility (SSR)

Dave King

Global energy consumption

Global energy consumption is expected to double by 2050 and triple by 2100.

Urgent demand for increased R&D effort!



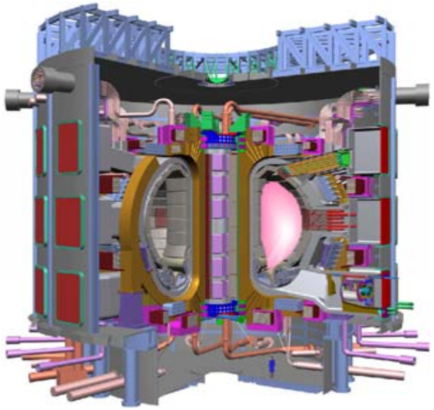
A change for energy and environment related research in the 21st century

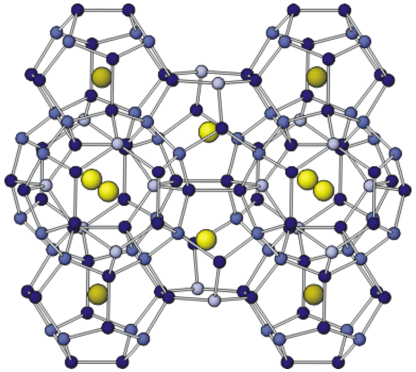
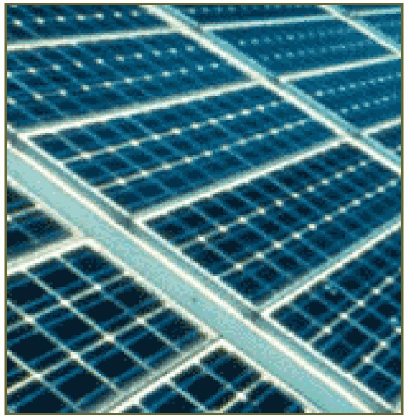
Energy strategy in the 21st century

Improve energy efficiency…

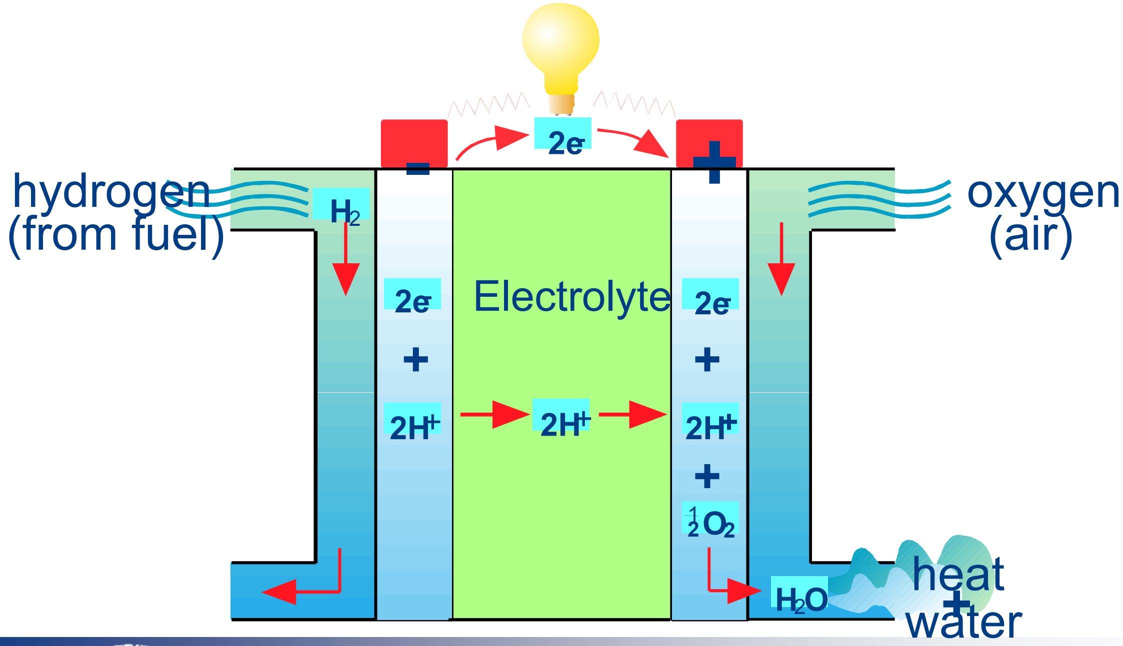
…and develop a diverse mix of zero carbon sources





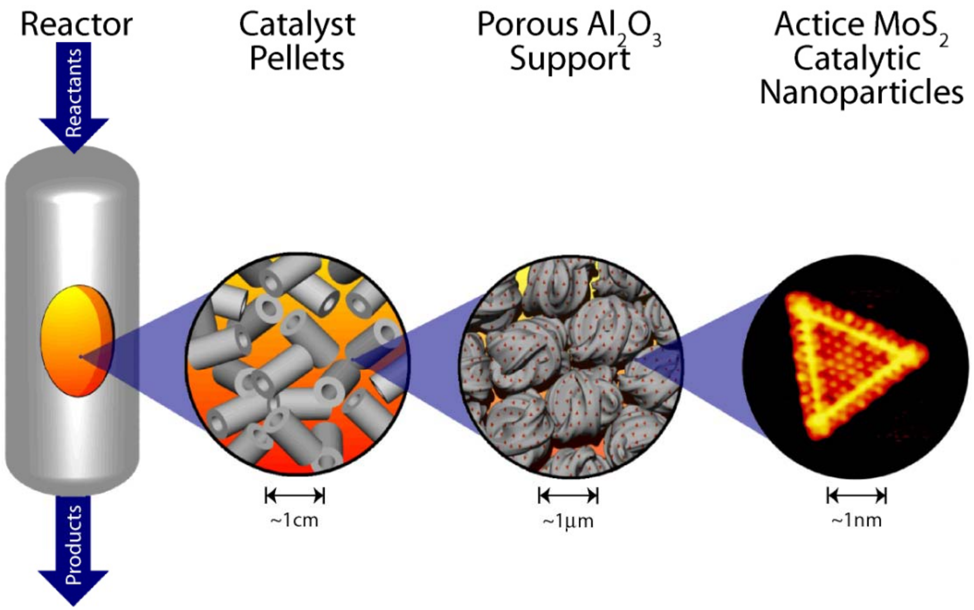





Nano-Catalysis is more important than ever: Green Energy, Green Fuel, Energy storage



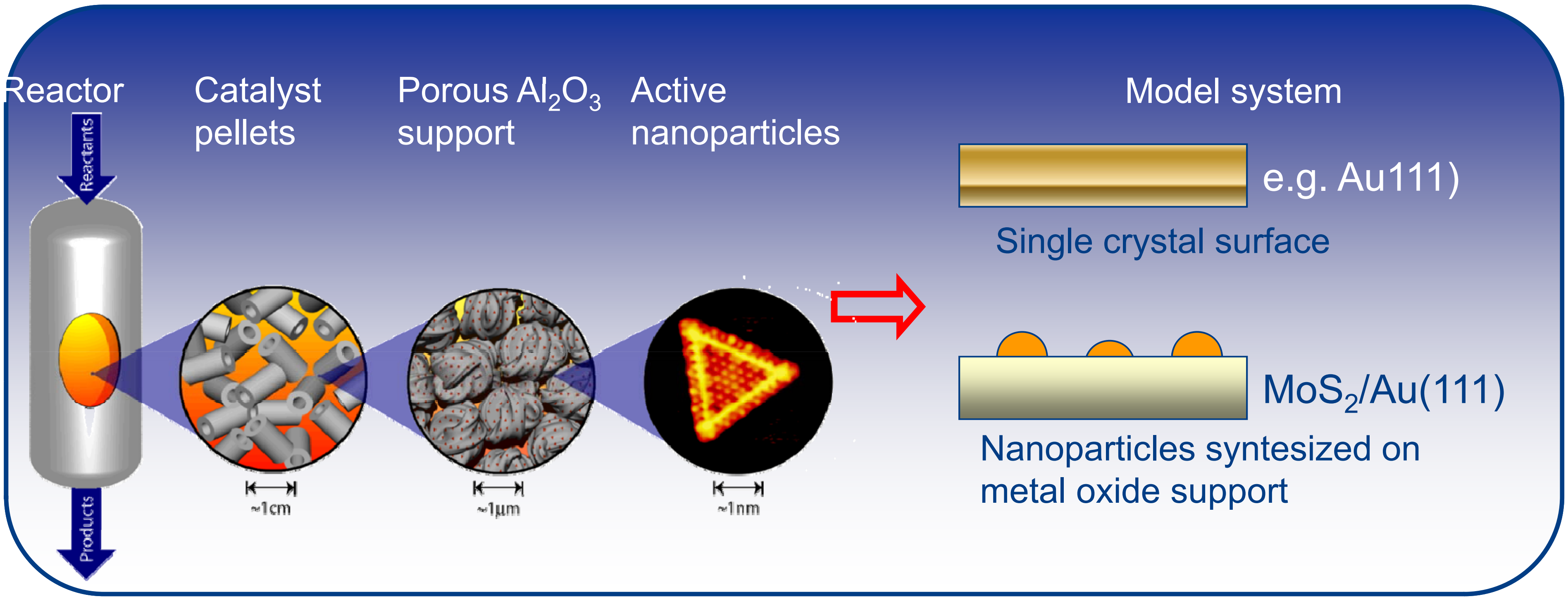
The Surface Science approach

Gerhard Ertl
Nobel Prize in 2007



The surface science approach –
The complexity of a catalyst is stepwise broken down into simplified problems which can be dealt with in details under well controlled conditions

Catalysis : The Surface science approach

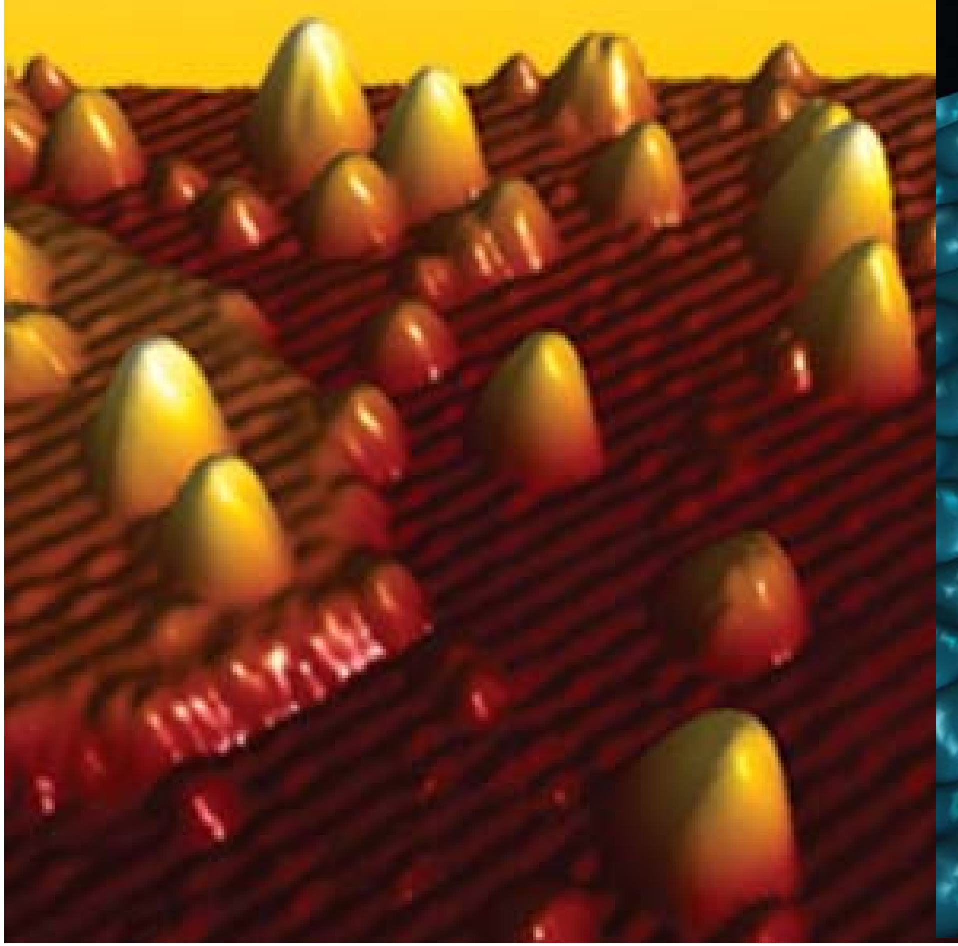


The complexity of a catalyst is stepwise broken down into simplified problems which can be dealt with in details under well controlled conditions

Size Matters

Au$_n$ on TiO_2(110)

Science 315, 1692 (2007)



Scanning tunneling microscopy: The ”Aarhus STM”™

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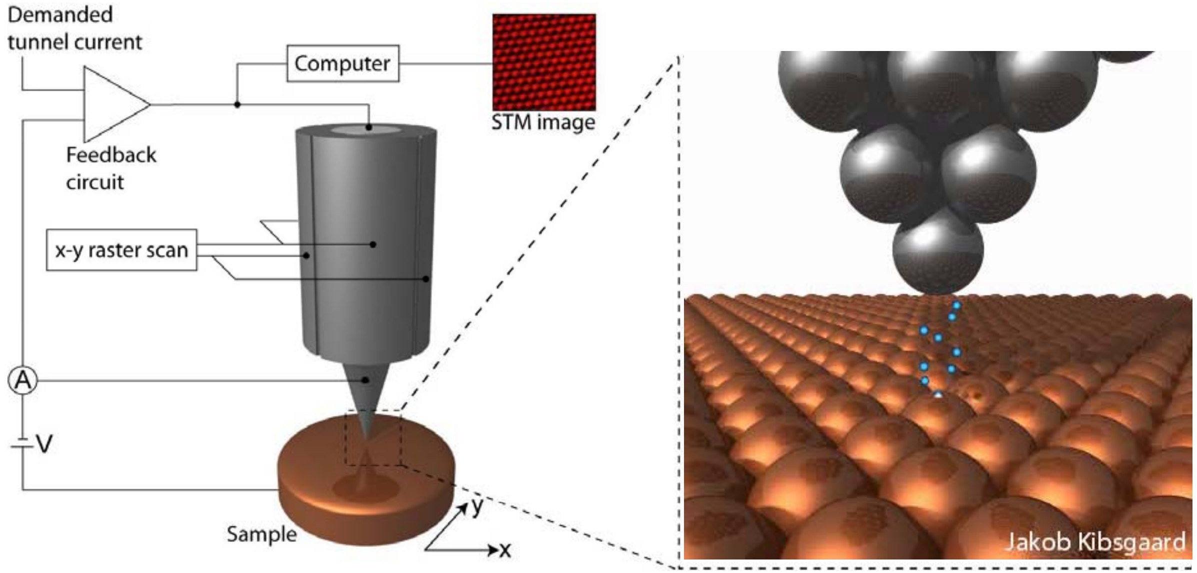

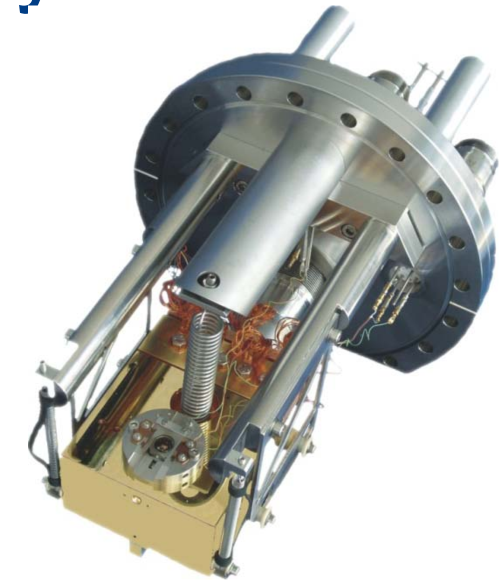

www.specs.de
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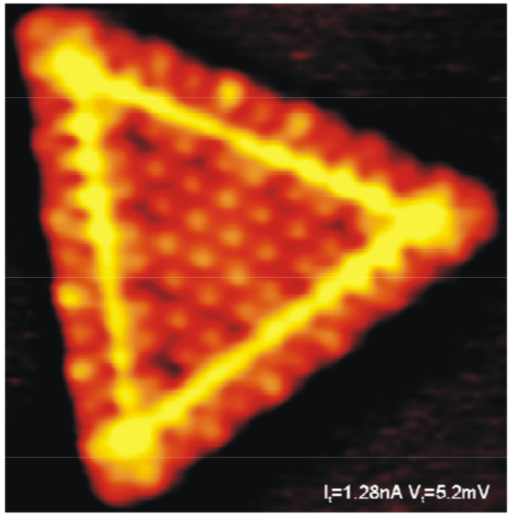
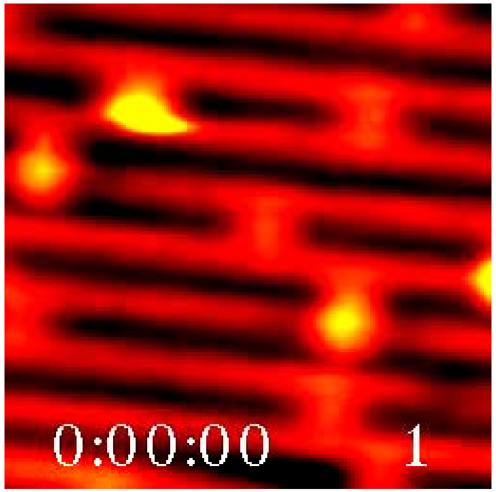
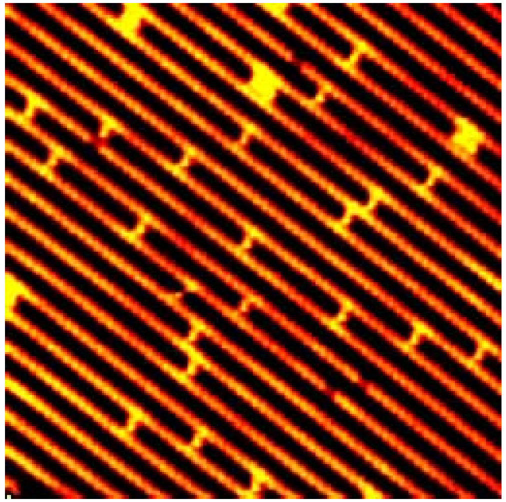
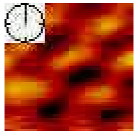


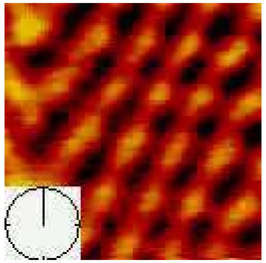


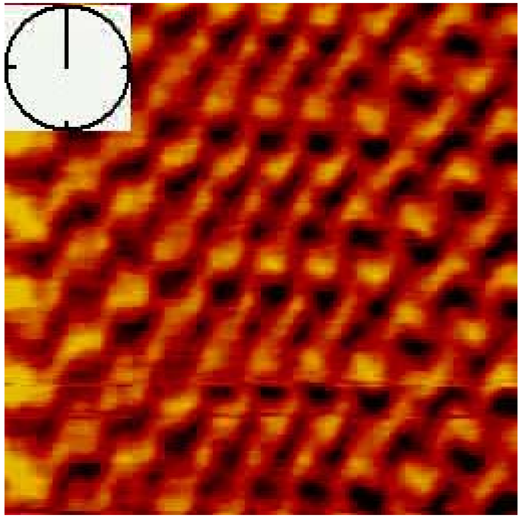


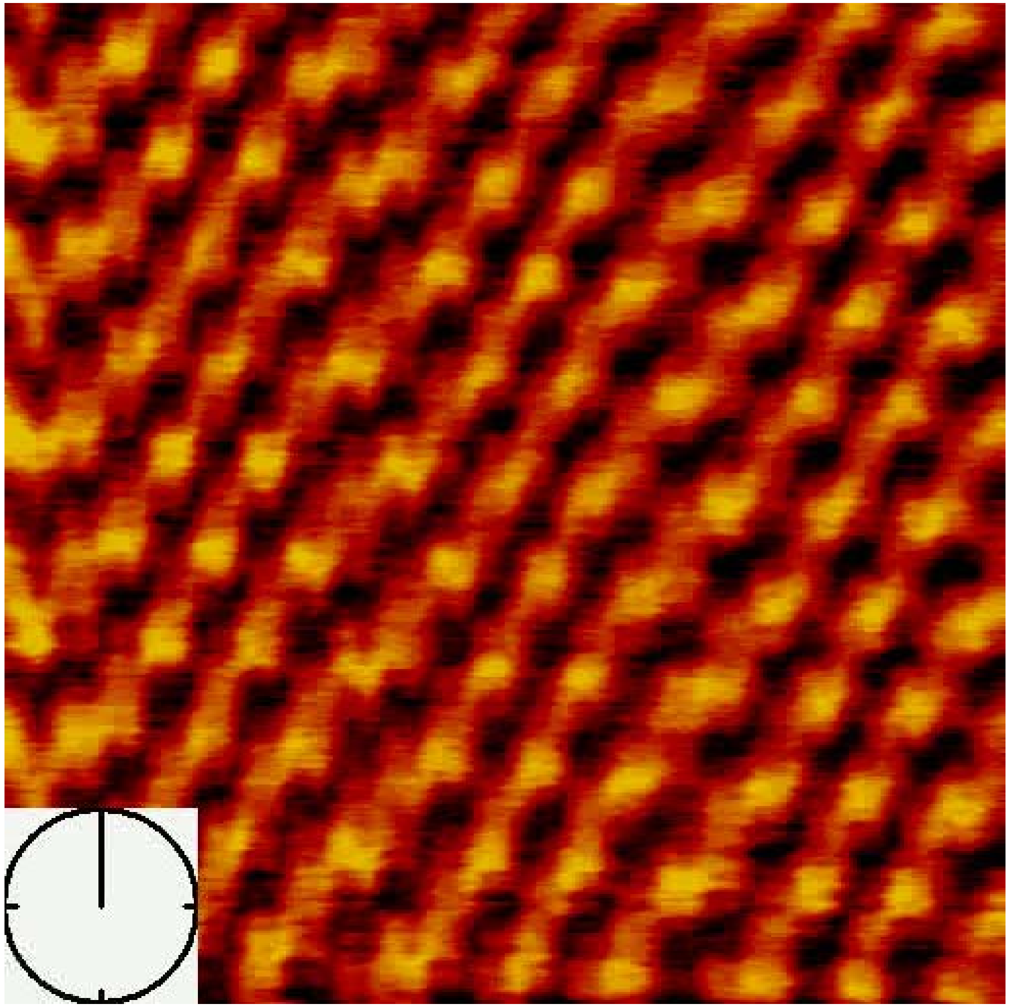
Examples of video rate STM movies

Atom-resolved
Video-rate STM

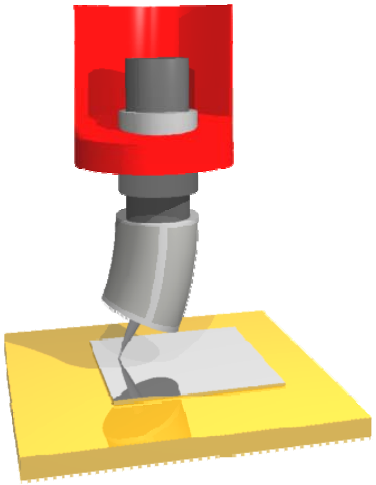


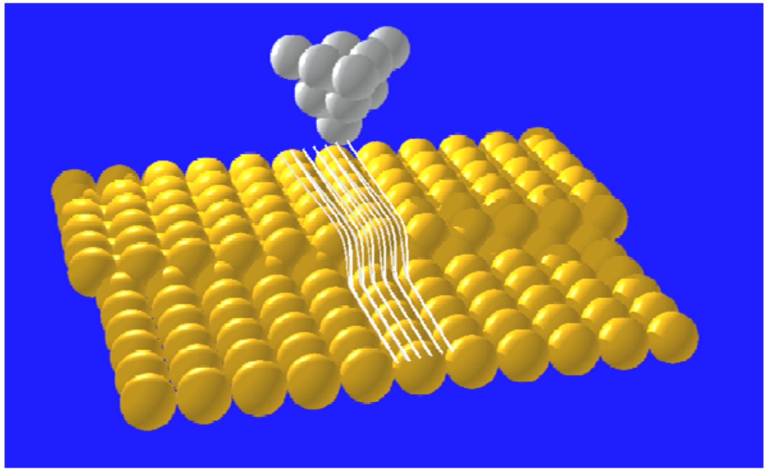






Scanning Tunneling Microscopy





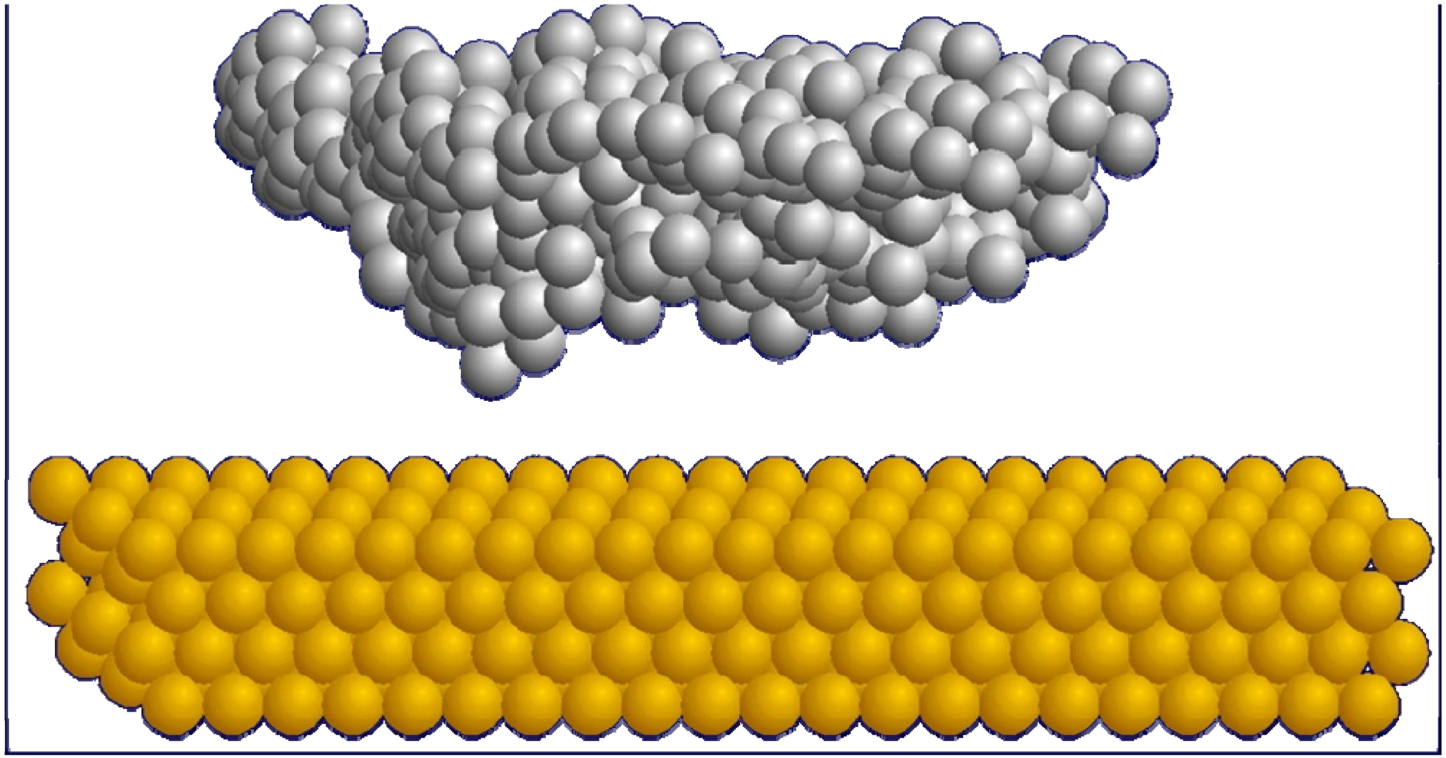
Tersoff-Hamann: $$I_t \propto V_t \sum_{\nu} |\psi_\nu(\overrightarrow{r_0})|^2 \, \delta(E_\nu - E_F)$$

Contour maps of constant Local Density of States (LDOS) at the Fermi Energy (E_F)

Metal surfaces : Geometric Structure

Oxides, Sulfides, Adsorbates : Geometric and Electronic Structure

STM principle



Towards atom-scale design of new Catalysts for Hydrogen production

- Steam Reforming of natural gas :

  $CH_4 + H_2O \qquad 3\,H_2 + CO$

  $(CO + H_2O \qquad H_2 + CO_2)$

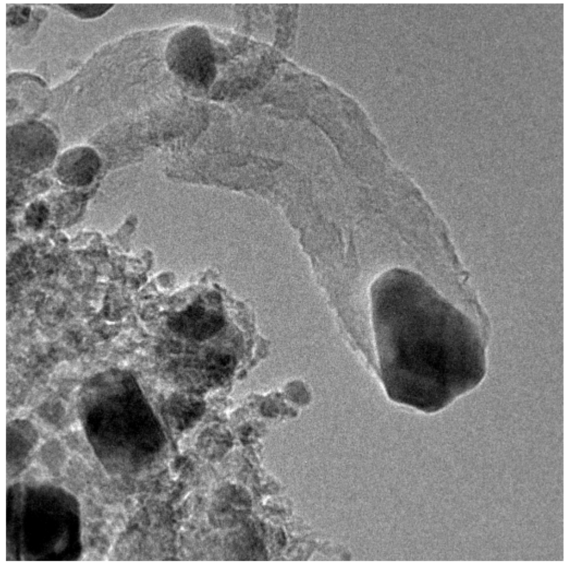
- Industrial Conditions :

  High Pressure (20 -50 bars)

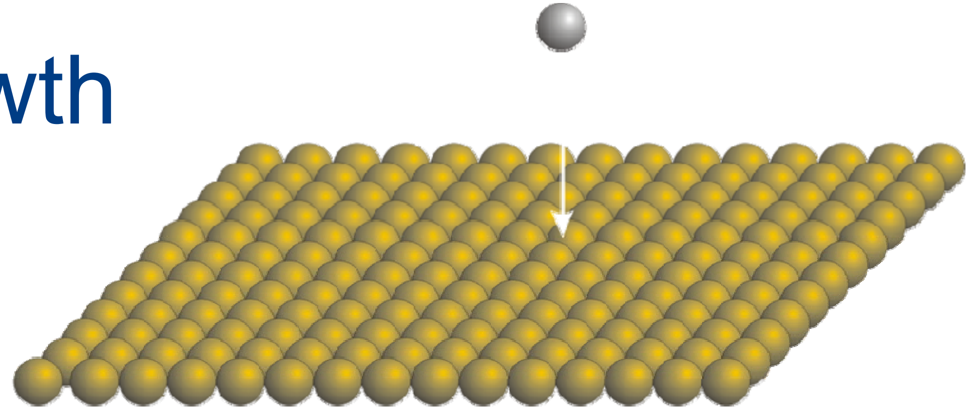
  High Temperature (500-1000 °C)

  Small metal particles dispersed on ceramic support

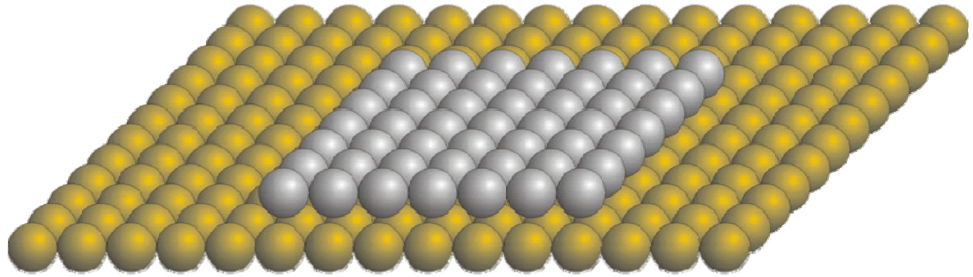
- High carbon activity leads to graphite formation



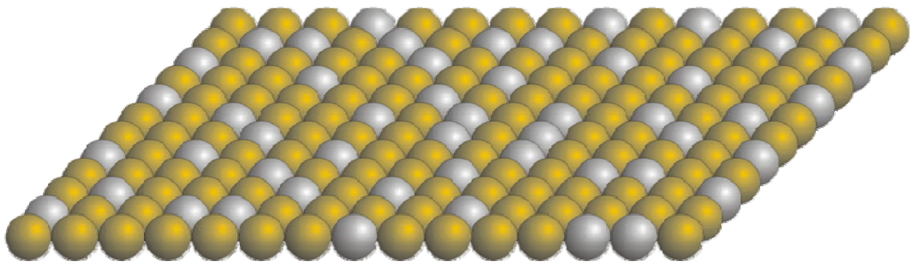
Metal-on-metal growth



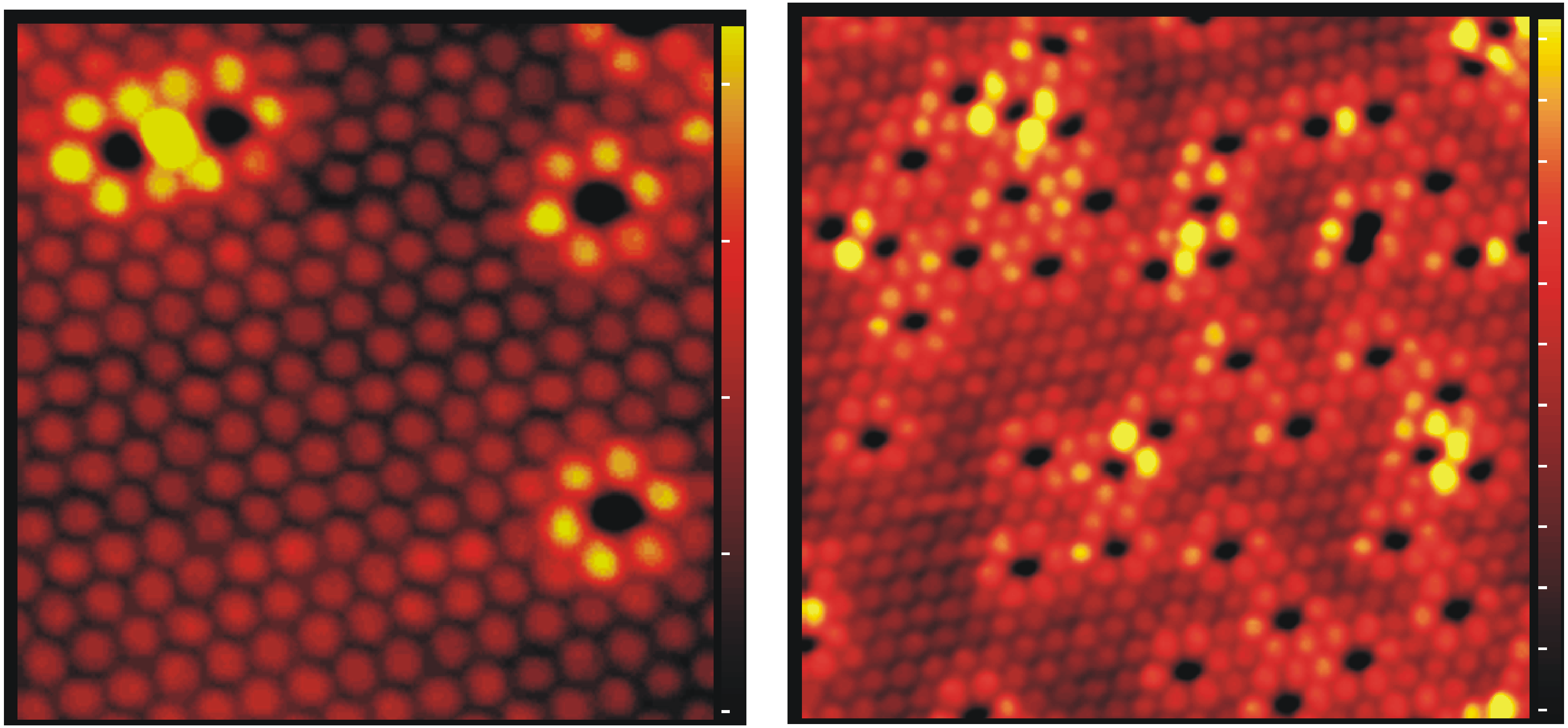
Island Formation



Binary Alloy
Au-Ni(111)

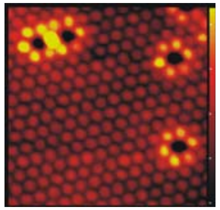


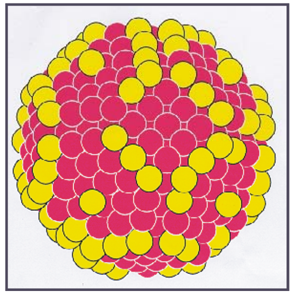
Au-Ni surface alloy:
A new steam reforming catalyst

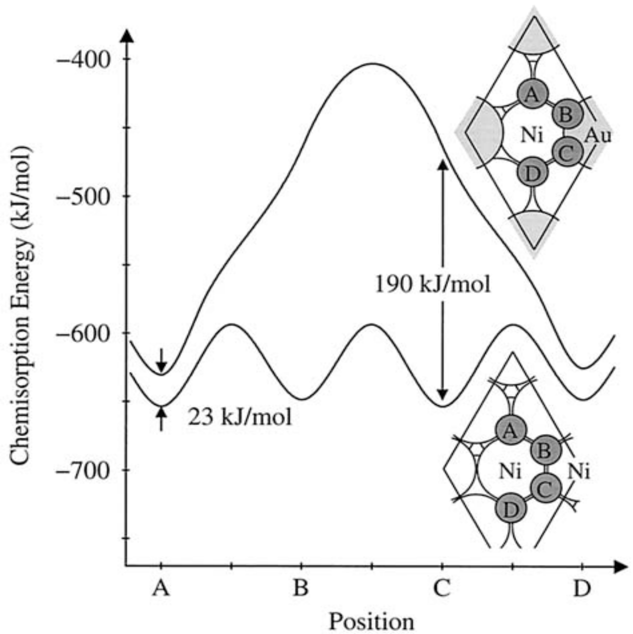


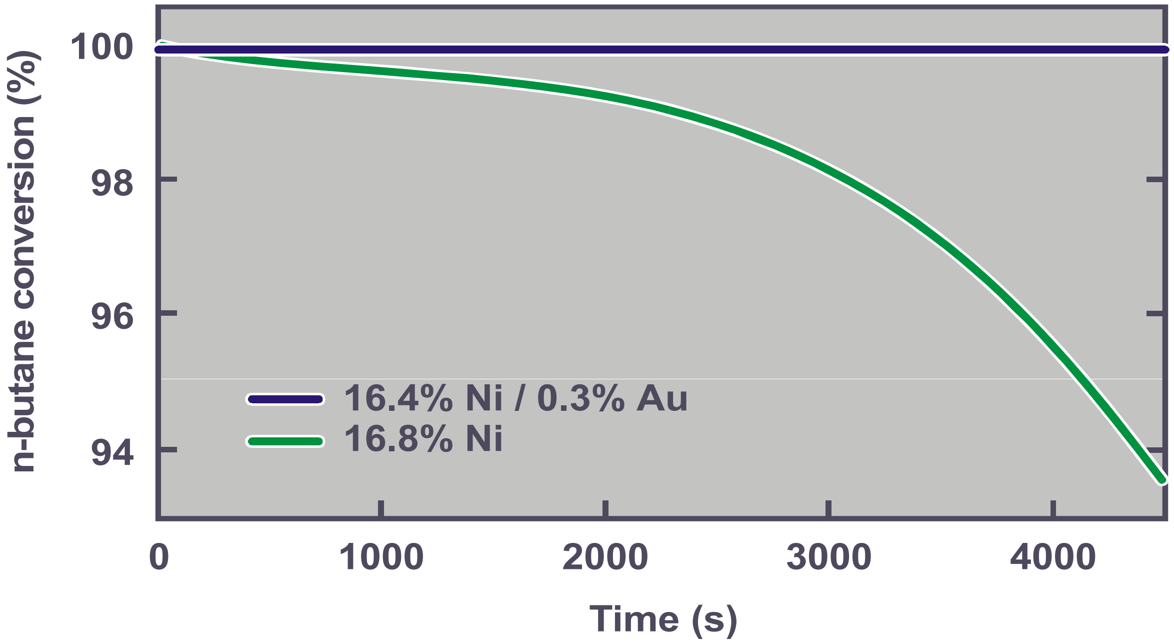
Besenbacher et al Science **279**, 1913

Design of a new catalyst based on the surface science approach



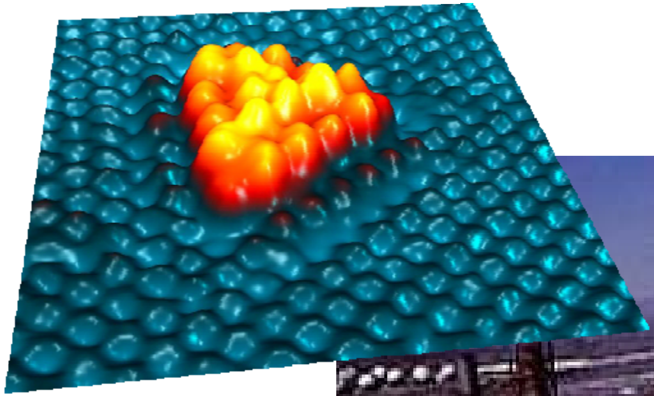






Besenbacher, Chorkendorff, Clausen, Hammer, Moelenbroek, Nørskov and Stensgaard, Science **279**, 1913

MoS_2-based hydrotreating model catalysts



GASOLINE

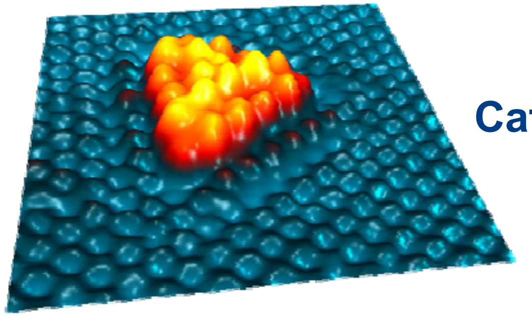
DIESEL

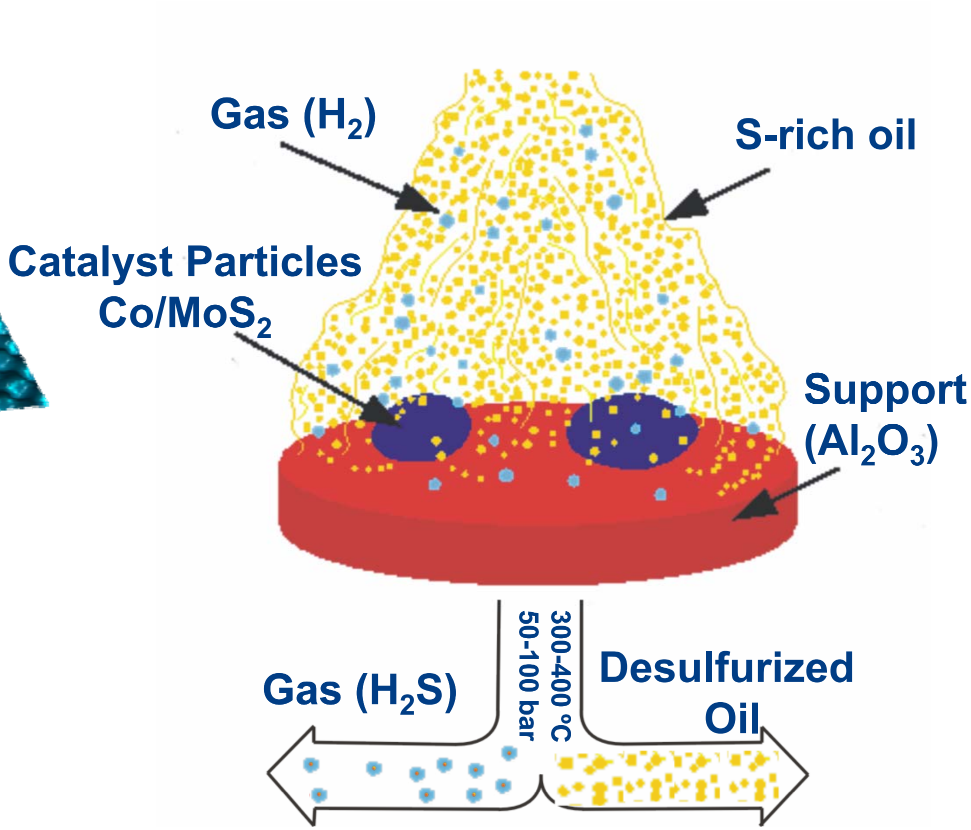
FUELS

CRUDE OIL

Refinery

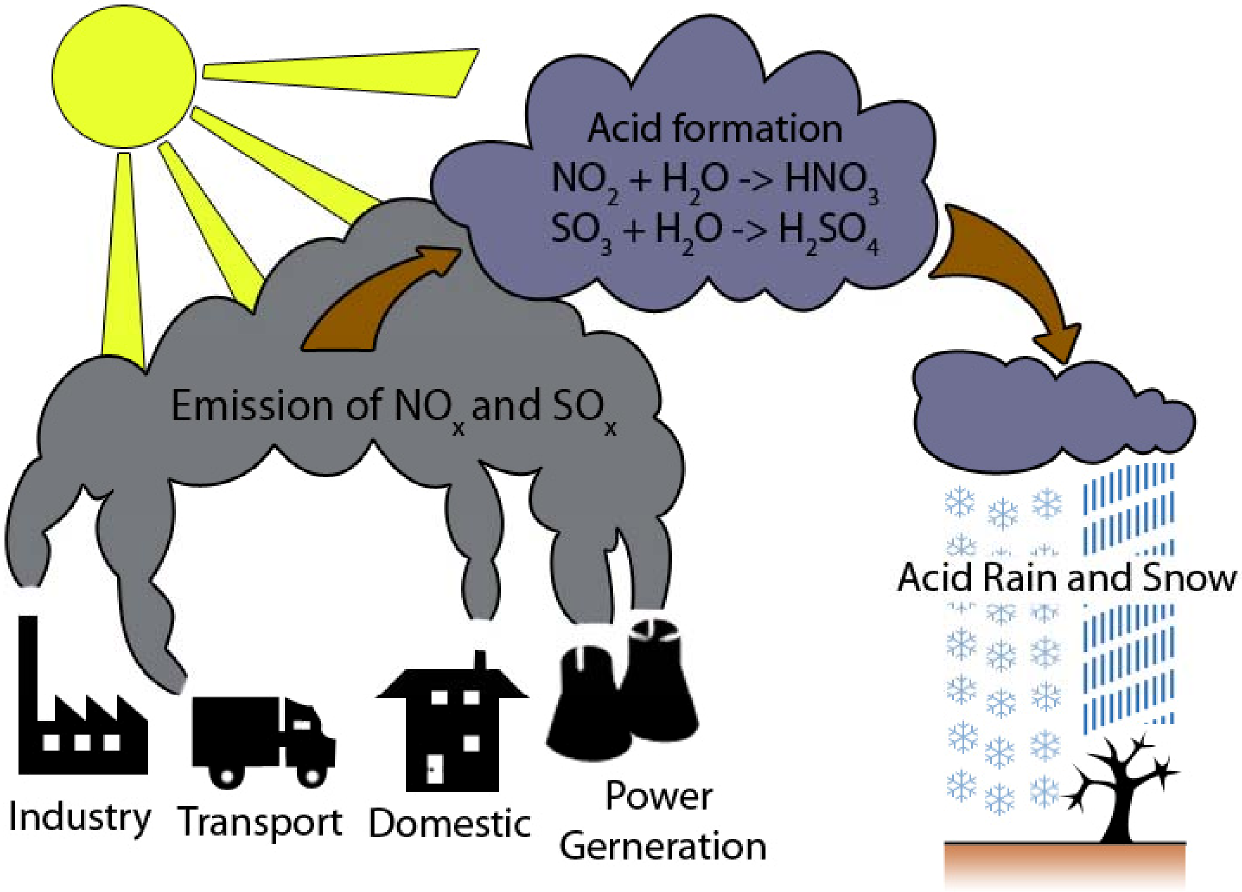
HydroDeSulfurization Catalysis (HDS)



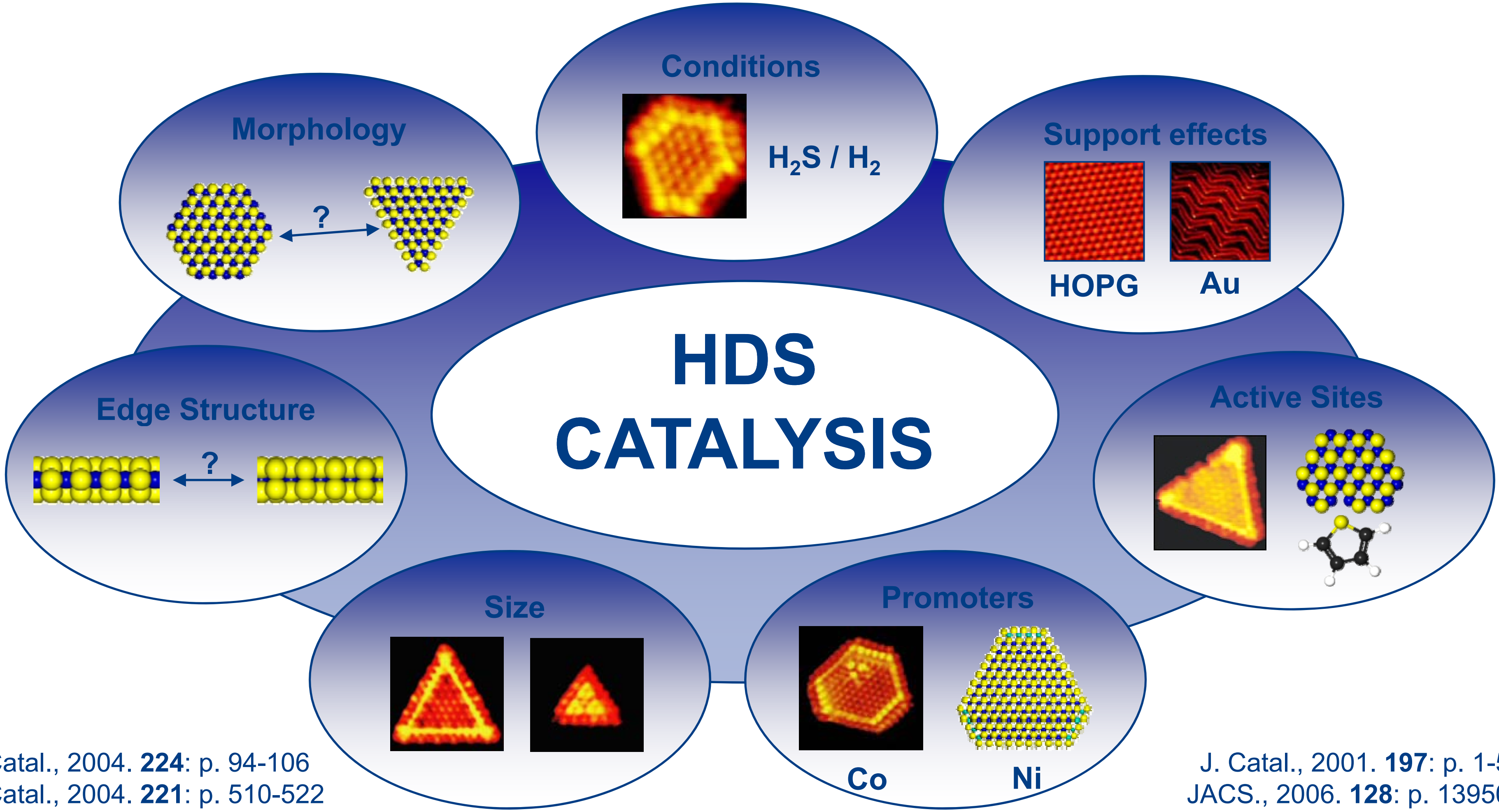


In-situ EXAFS measurements:
single-layer MoS_2-like ~1-3 nm at 400 ºC

Hydrodesulfurization - (HDS)
Sulfur emission => acid rain



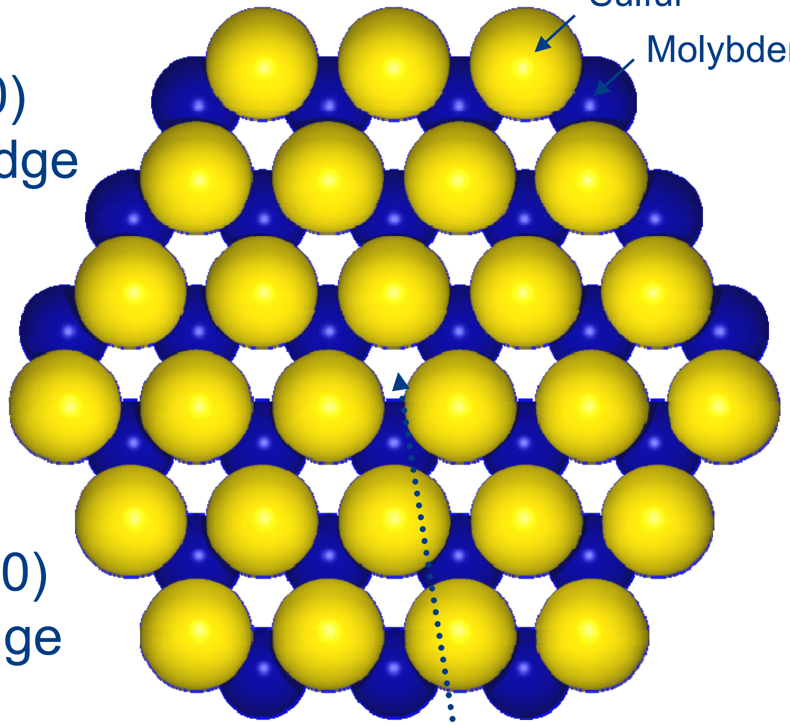
Fundamental questions in HDS

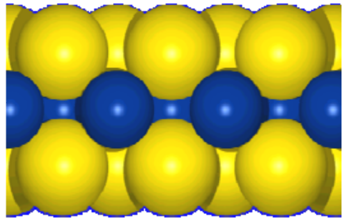


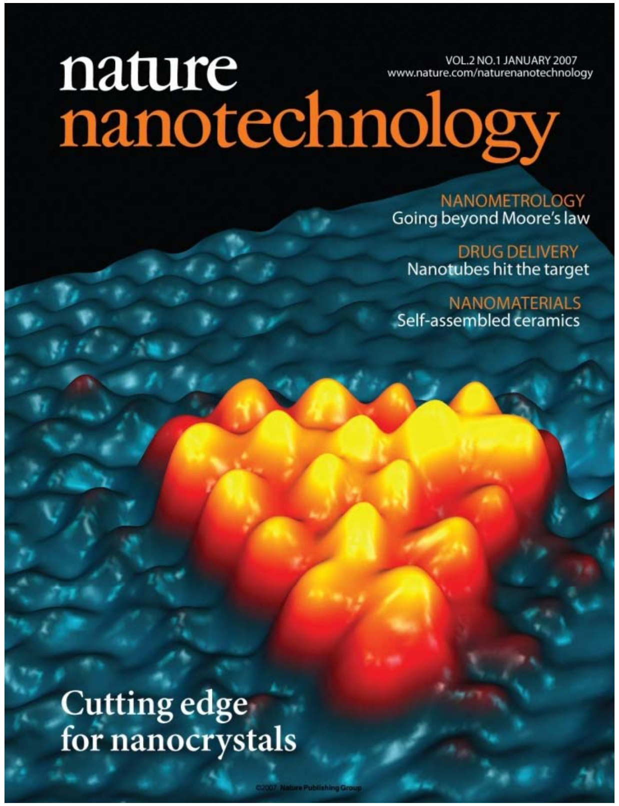
J. Catal., 2004. **224**: p. 94-106
J. Catal., 2004. **221**: p. 510-522
Adv. Catal., 2006. **50**: p. 97-143
Catal. Today, 2006. **111**: p. 34-43
Nature Nanotechnology, 2007. **2**: p. 53-58

J. Catal., 2001. **197**: p. 1-5
JACS., 2006. **128**: p. 13950
J. Catal., 2007. **249**: p. 220-233
Nanotech., 2003. **14**: p. 385-389
Phys. Rev. Lett., 2000. **84**: p. 951-954

Nano-clusters of MoS_2



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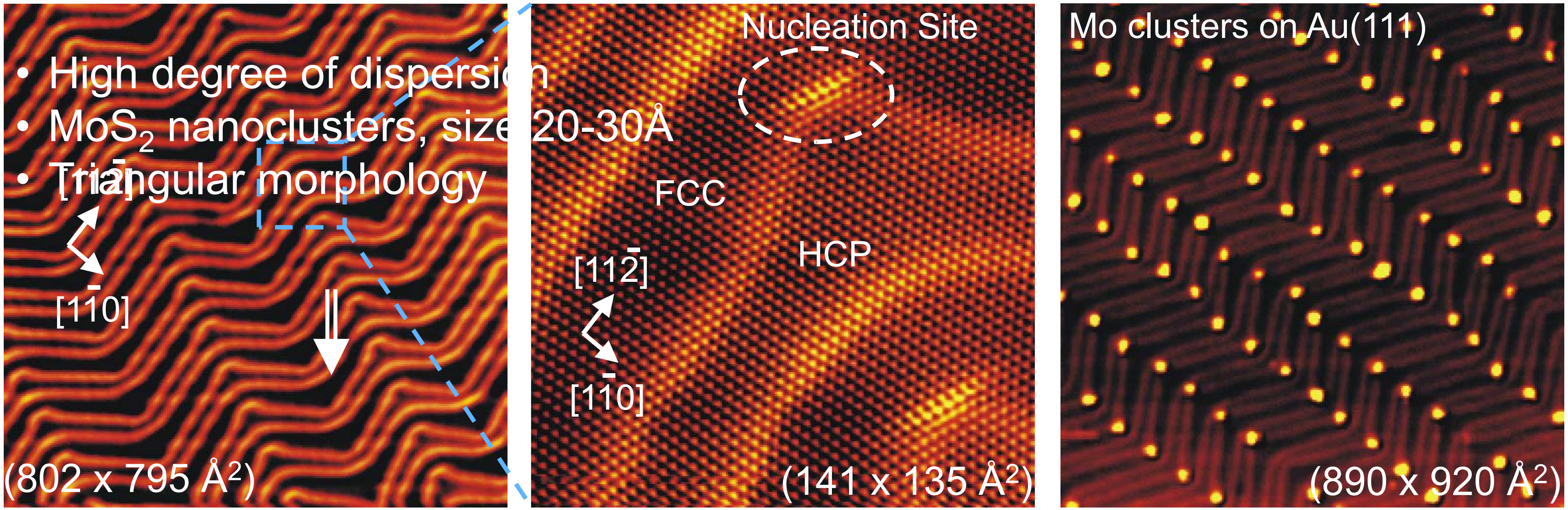
Self-assembled ceramics
Cutting edge
for nanocrystals

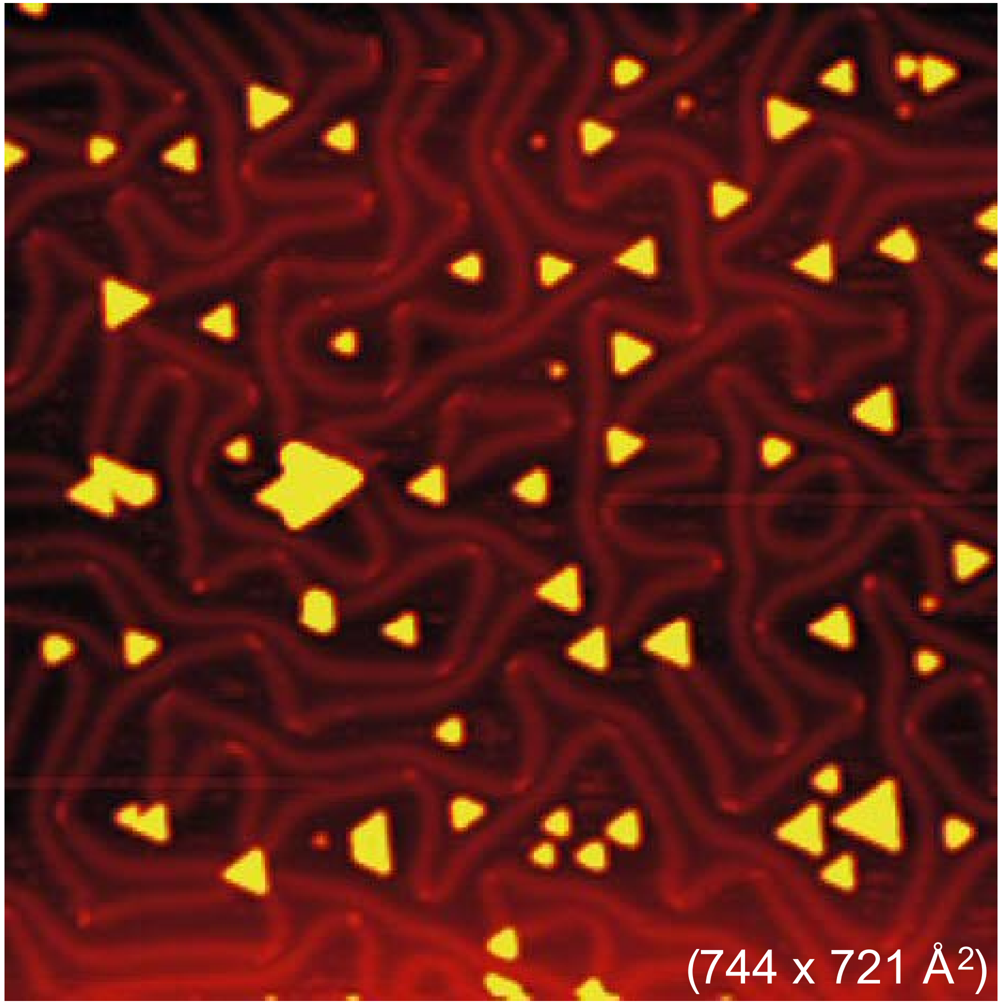
Model substrate: The Au(111) surface

- High degree of dispersion
- MoS_2 nanoclusters, size 20-30Å
- Triangular morphology



Good model system for a HDS catalyst

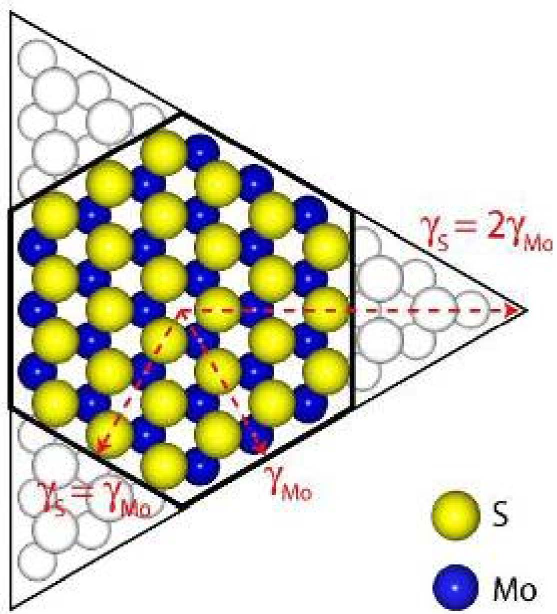
Model substrate: The Au(111) surface

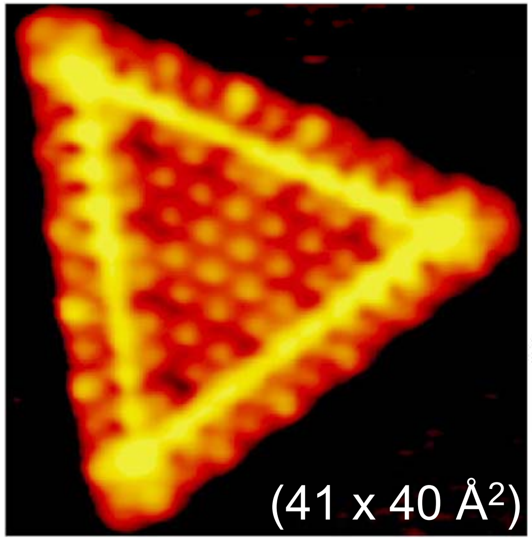


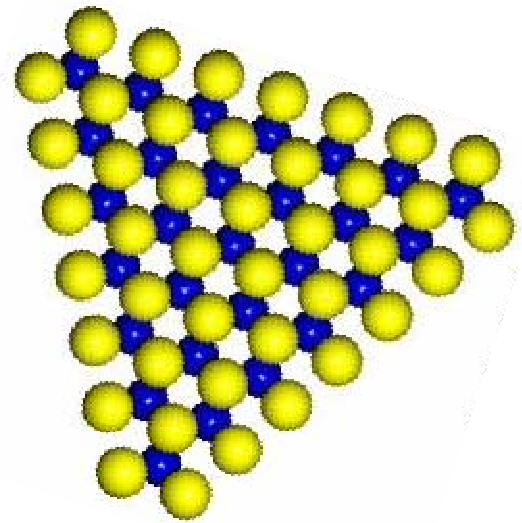
MoS_2 nanoclusters

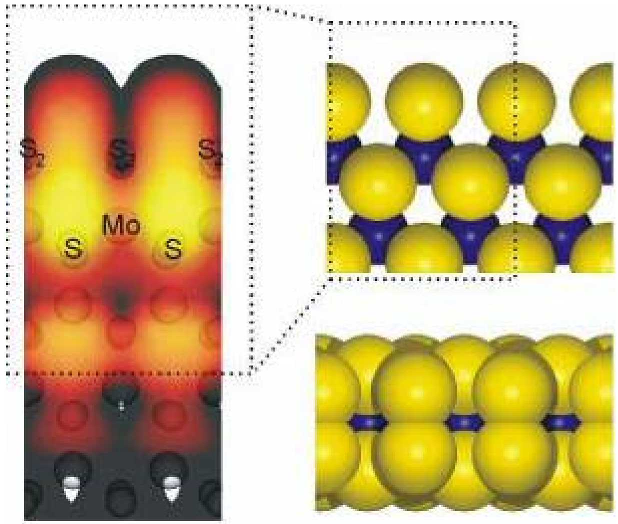
The distinctive features of the MoS_2 nanoclusters are:

- Triangular shape
- Single S-Mo-S layer (Height: 3.16Å)
- One-dimensional metallic edge state, resulting in the observed bright brim along the edge



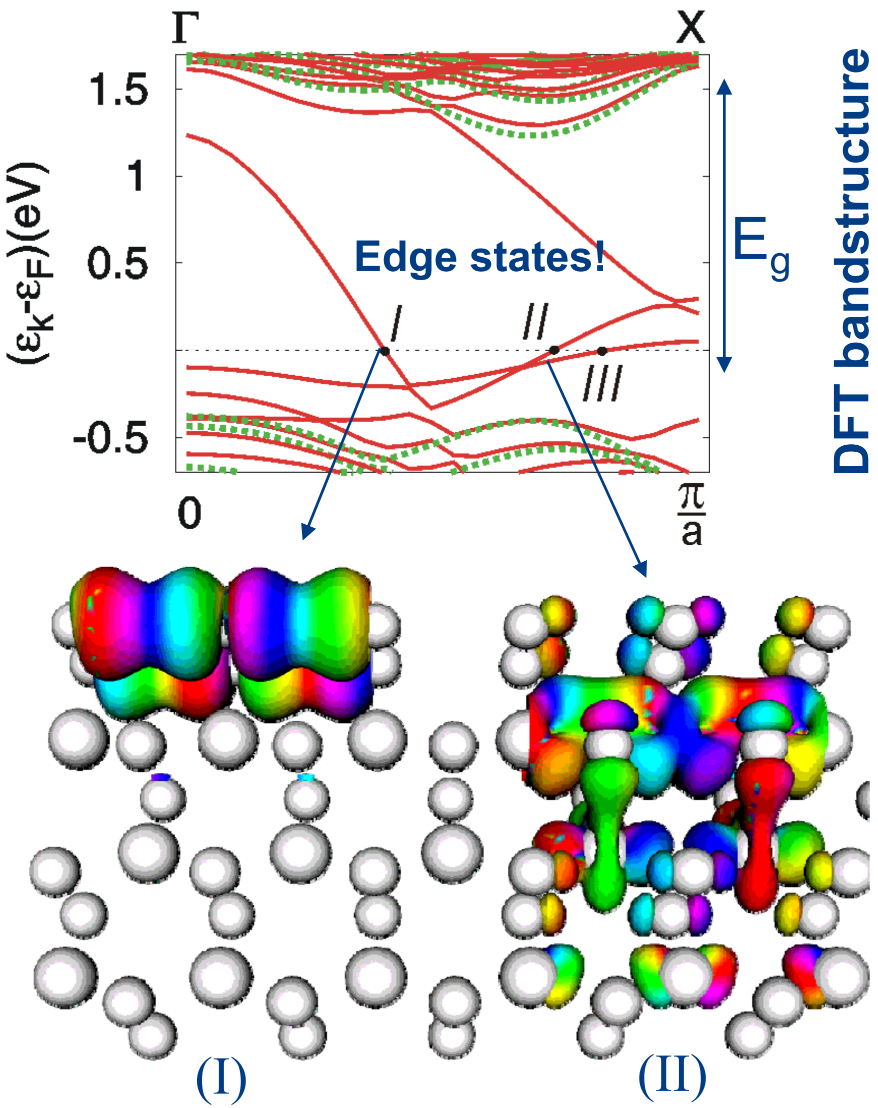


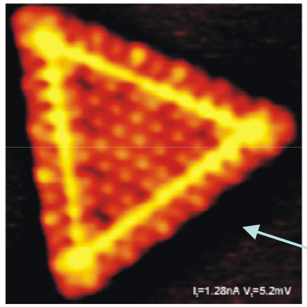




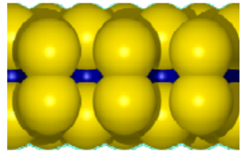
J. V. Lauritsen and F. Besenbacher, Adv. Catal. 50, 97 (2006)
S. Helveg, J. Lauritsen, F. Besenbacher *et al.* PRL 84, 951

Metallic Edge-states in MoS_2





Mo edge with
S dimers (100%)



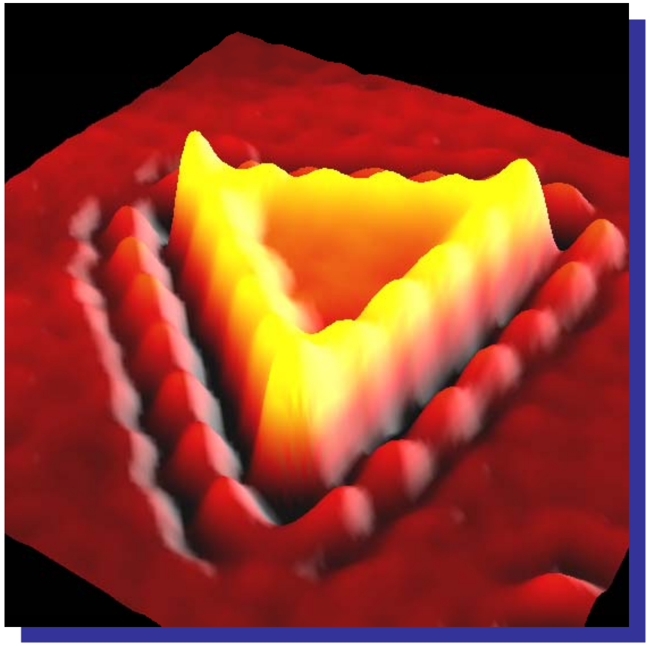
- Bulk MoS_2 **semiconductor** E_g=1.23eV
- Edges in MoS_2 triangle are **metallic**

<u>Metallic edge states</u>

(I) Localized on S-dimers on Mo-edge.
(II) Extending over the first three rows.

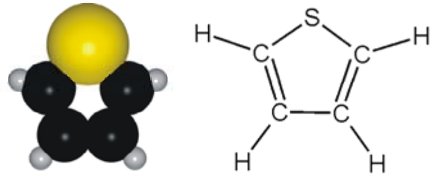
Bollinger, Lauritsen, Jakobsen,
Nørskov, Helveg, Besenbacher
Phys. Rev. Lett. **87** 196803

Thiophene adsorption on MoS_2 Nanoclusters

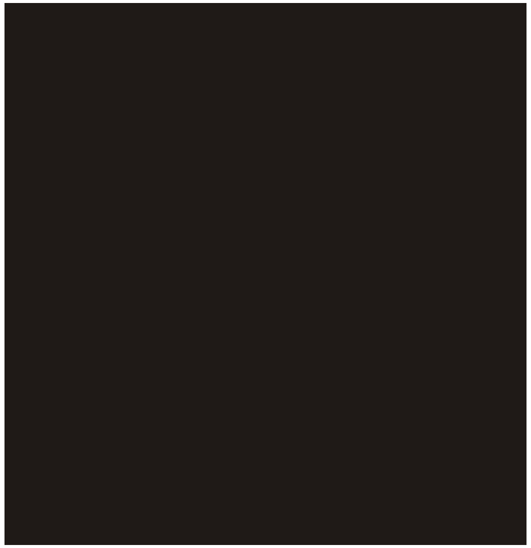


HDS test molecule

Thiophene (C_4H_4S)



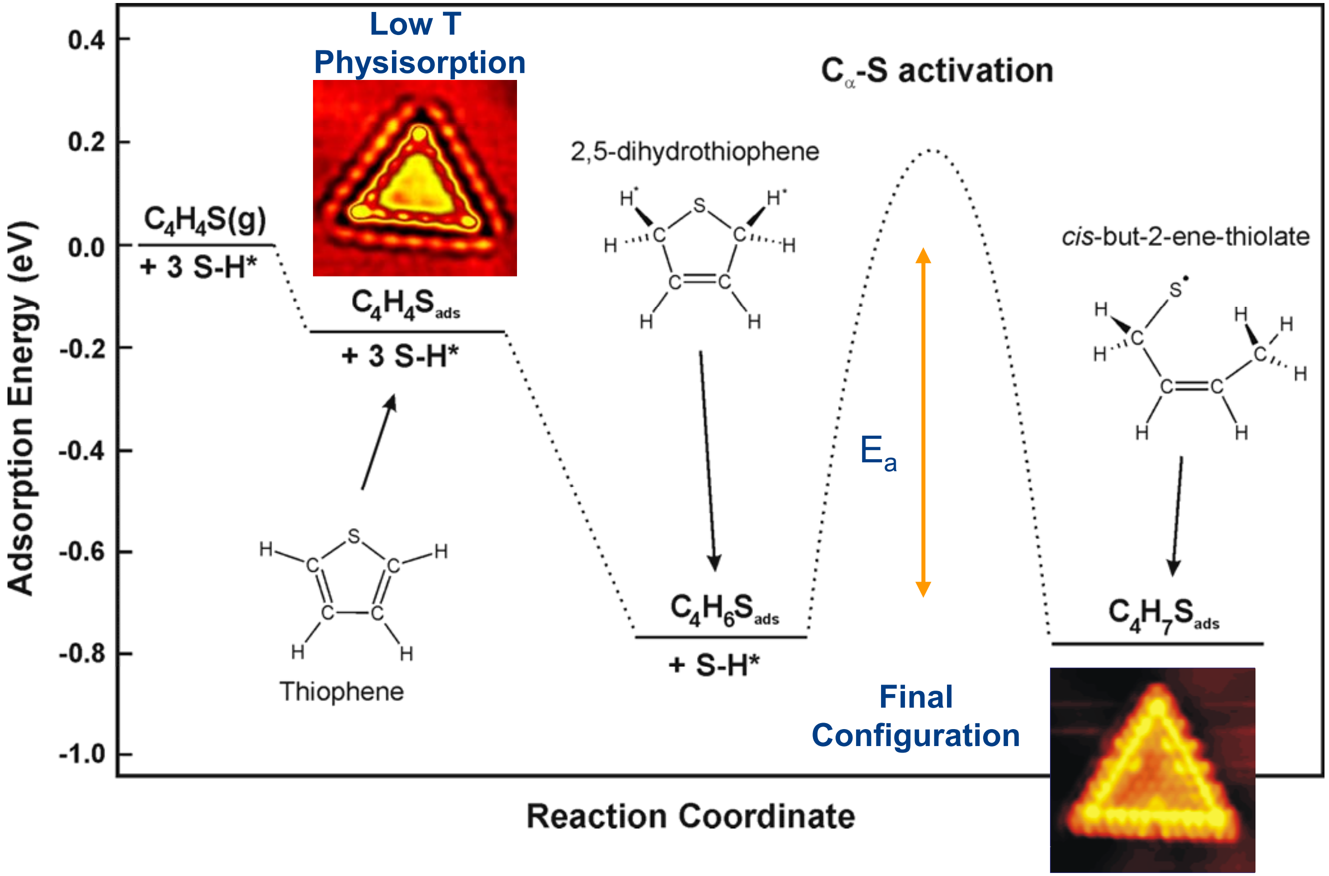
VdW Size ~ 4 × 5 Å^2



Thiophene adsorbed on top of BRIM sites

J.V. Lauritsen et al. Nanotechnology 14, 385 ; J. Catal. 224, 94

Reaction of Thiophene – Energetics (DFT)



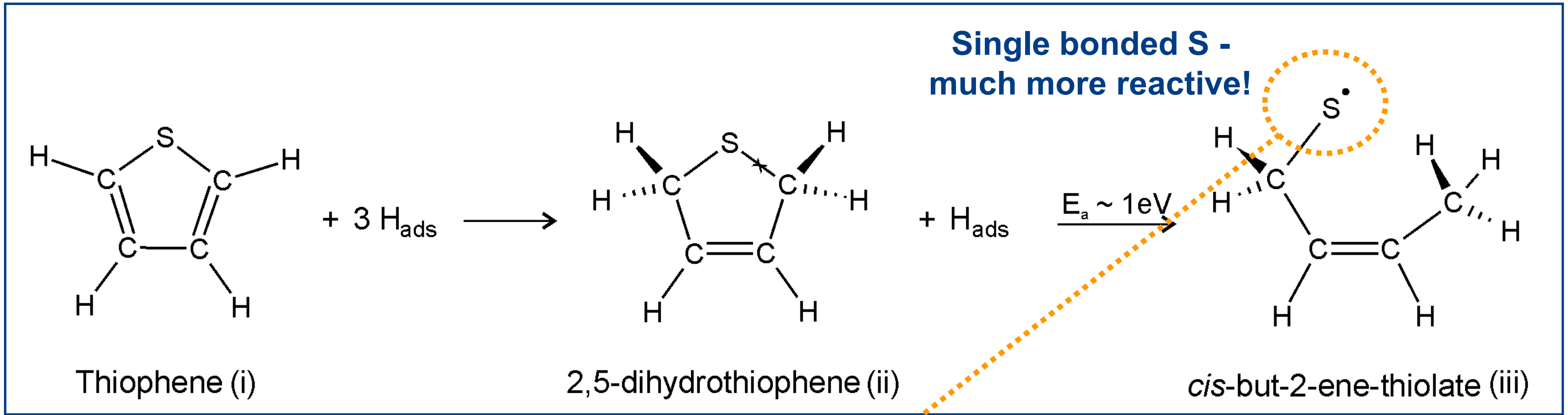
Activation barrier $E_a \approx 1$ eV $\Rightarrow$

Reaction rate = $10^{13} \cdot \exp(E_a/kT) \approx$ <u>10^5 reactions/sec</u> at 673 K

J.V. Lauritsen, M. Nyberg *et al.* Nanotechnology **14**, 385 (2003)
Journal of Catalysis **221**, pp. 510-522 (2004)

First step of HDS of Thiophene

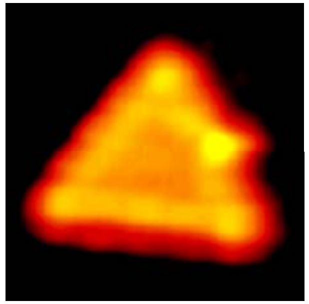
Occurs on unusual active sites associated with the one-dimensional metallic edge states in MoS_2



Thiophene physisorbed on cluster (E_{ads} = -0.2eV)

dihydrogenated thiophene - double bond flips over

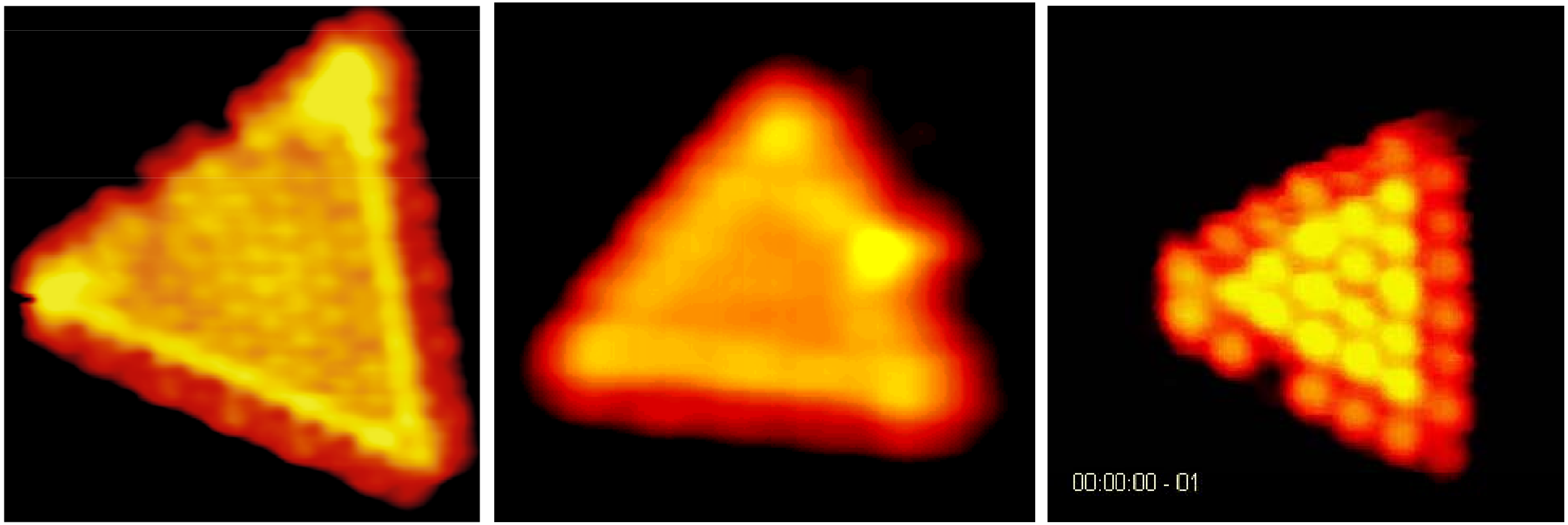
Intermediate adsorbed on cluster observed with STM



Next step:
Under reaction conditions S vacancies will be abundant
Final S extrusion of the thiolate may easily occur here

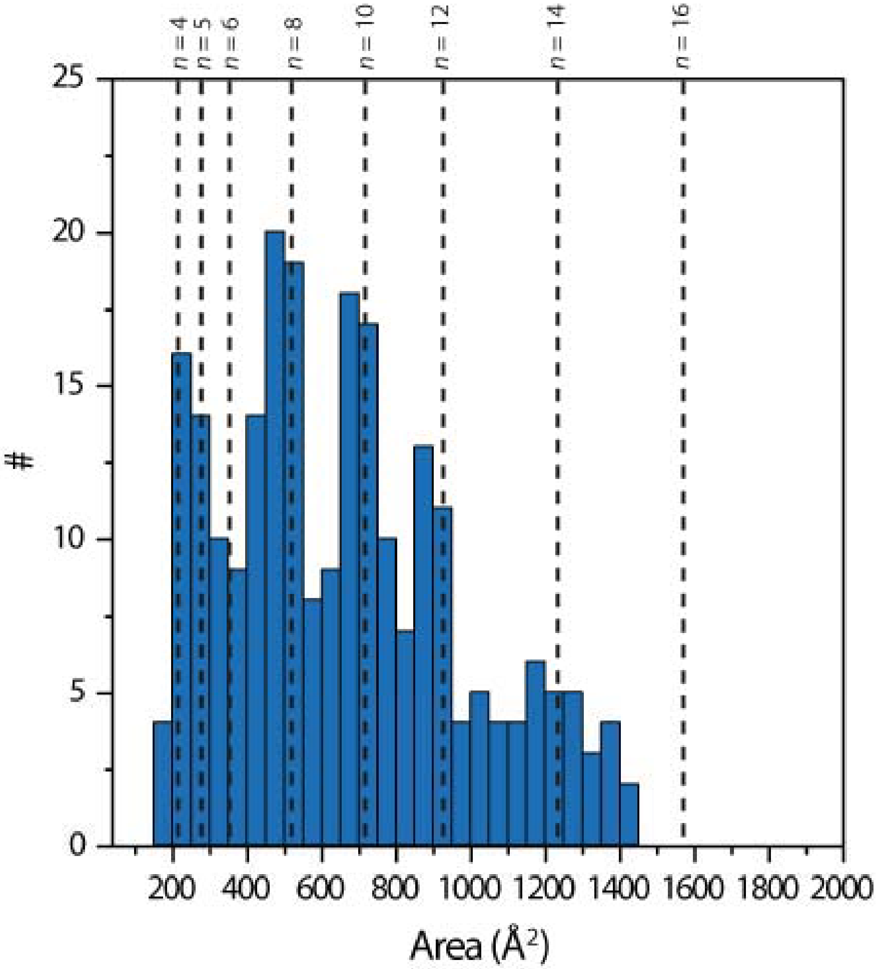
J.V. Lauritsen *et al.* Nanotechnology **14**, 385 (2003)
Journal of Catalysis **221**, pp. 510-522 (2004)

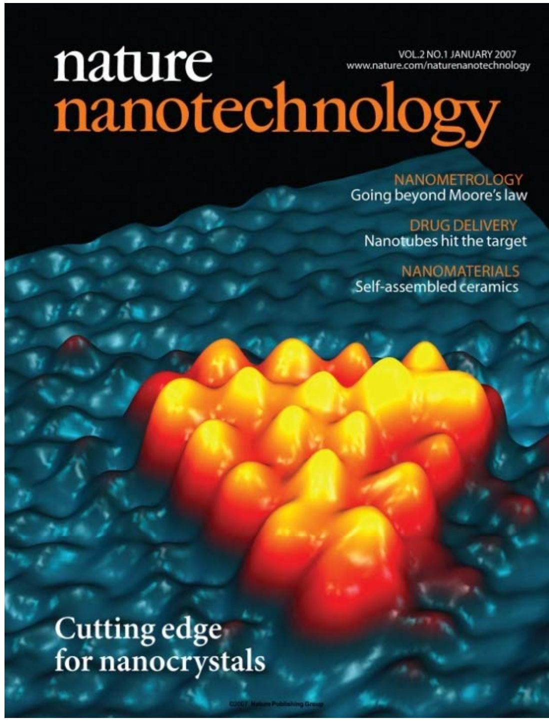
Final HDS Pathway Involves Edge Vacancies

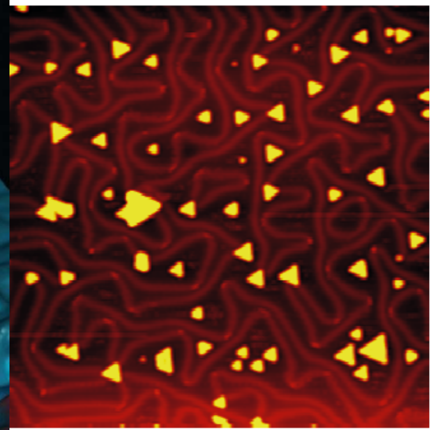


J.V. Lauritsen et al. Jour. Catal. 224, 94

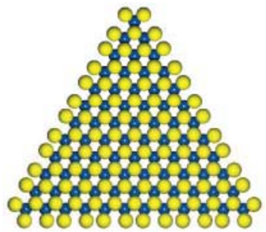
MoS_2 : Cluster size distribution







"Magic" clusters:

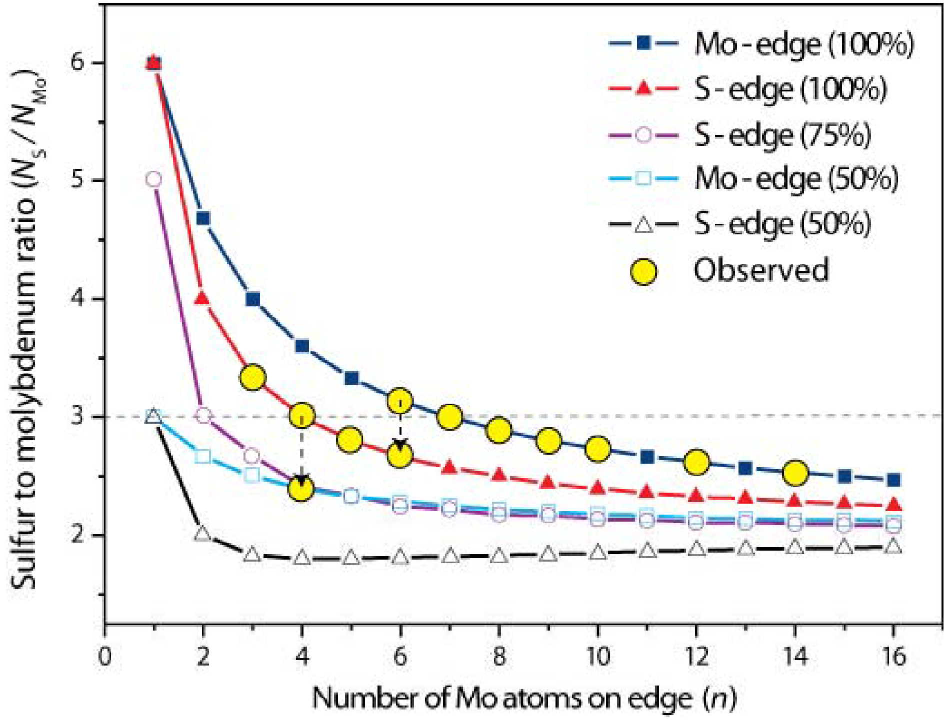


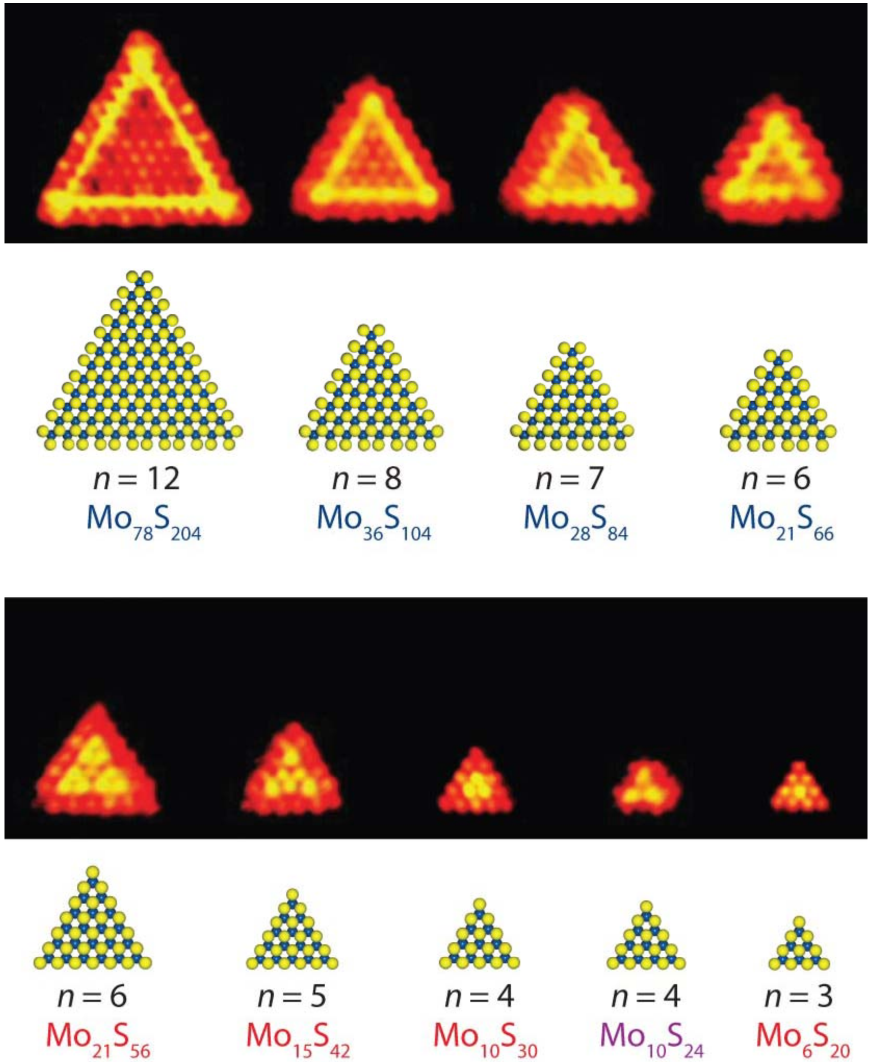
<u>$n > 6$:</u>
8,10,12,14….

<u>$n \leq 6$:</u>
3,4,5,(6)

J. V. Lauritsen, Besenbacher *et al.* Nature Nanotechnology, 2, 53

MoS_2 Cluster Stoichiometry vs. size





Clusters with a S:Mo stoichiometry of more than ~3 are not favored

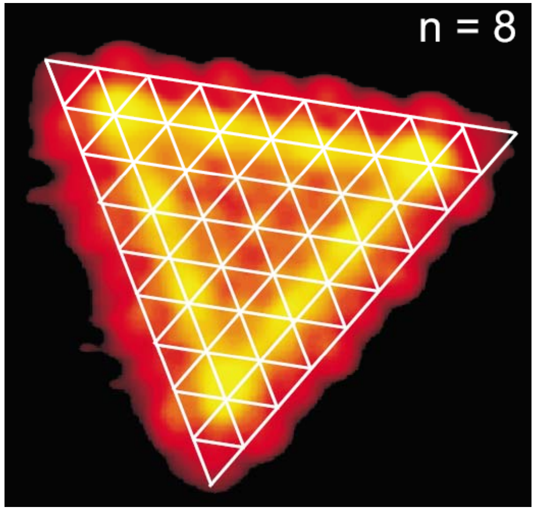
⇓

Two effects determine the edge termination:

- Lowering of the edge free energy
- Reduce the sulfur excess.

J.V. Lauritsen, J. Kibsgaard, F. Besenbacher *et al.*
Nature Nanotechnology 2 (2007) 53-58

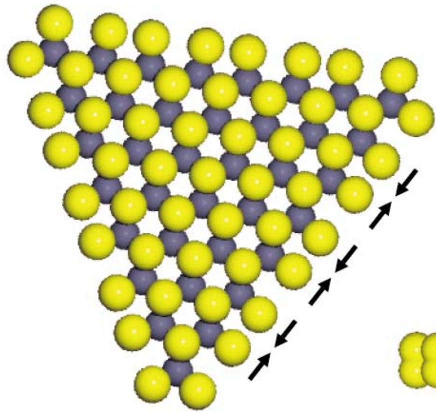
Detailed edge analysis



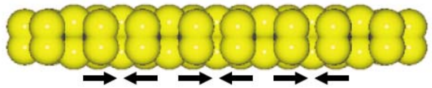
- Edge protrusions out of registry
- Intensity variation
- Paring of S_2 dimers

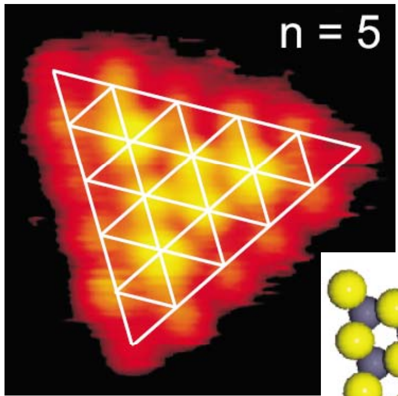
⇓

Even n favored



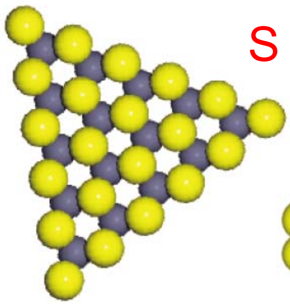
Mo edge (100%)



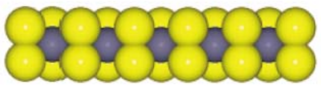


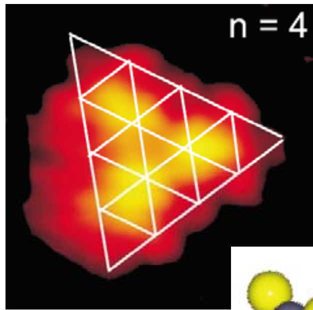
- Edge protrusions in registry
- No intensity variation

⇓



S edge (100%)



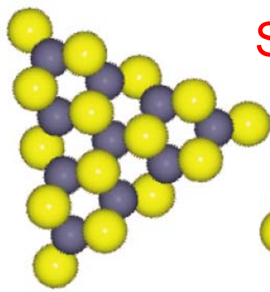


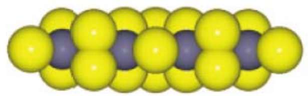
- Edge protrusions in registry
- Intensity variation

⇓

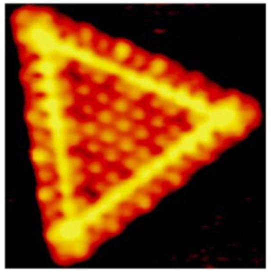
S edge (75%)

Sulfur vacancies

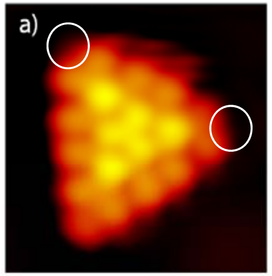




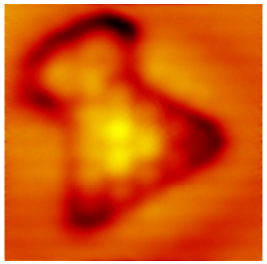
Take Home message



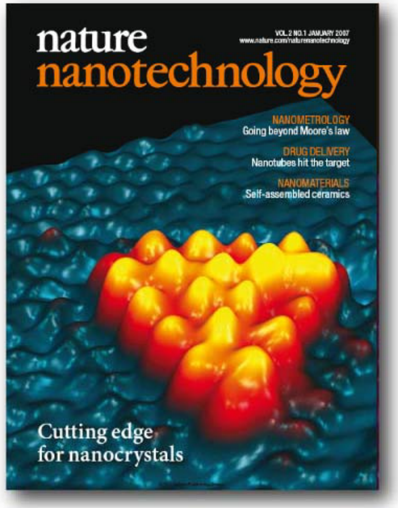
- STM provides insight into the atomic-scale structure of MoS_2 nanoclusters

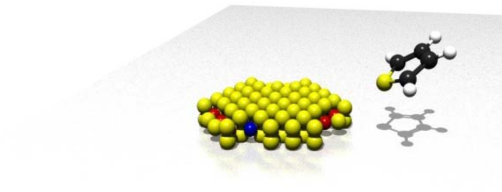


- STM images the active sites on the cluster edges, which are not resolved with other techniques



- Characterization of size-effects shows potential for improving the catalysts based on atomic-scale insight (nanocatalysis)





Brimming with activity

Per Zeuthen and Lars Skyum, Haldor Topsøe, Denmark, explain a new technology for high-activity hydroprocessing catalysts and present industrial experience highlighting their performance.

The need for high-activity hydroprocessing catalysts is more pronounced than ever. European refiners are ready to supply diesel and gasoline fuel with maximum 50 wt ppm sulfur from 2005 and maximum 10 wt ppm must be fully implemented from 2009. In a few countries, the near-zero level has already been introduced. As of June 2006, on-road diesel in the US must contain less than 15 wt ppm sulfur and gasoline less than 30 wt ppm sulfur.

Catalyst vendors respond to market demand by developing hydrotreating catalysts with significantly higher activity than previous generations of catalysts. With a trial-and-error catalyst development approach, it has been possible to achieve minor improvements, but obviously this is not the optimum way to develop high-activity catalysts. Topsøe's approach has therefore been to find a path from fundamental to applied research, and based on insight into HDS catalysis on the atomic scale, the company has in recent years succeeded in developing hydrotreating catalysts with considerably higher activities than previous generations of catalysts. In the 1980s and at the beginning of the 1990s, when hydrotreaters were operated at lower HDS conversion levels (up to 95 - 97%) than today (up to 99.95%), the sulfur removal primarily proceeded via the direct desulfurisation route. The primary objective of the research work at that time was to understand and develop catalysts with a high density of sites for direct desulfurisation. It was found that the activity correlated with the presence of Co-Mo-S (or Ni-Mo-S) structures on the alumina support. Also, it was shown that the sites responsible for the direct desulfurisation were sulfur vacancies located at the edges of the Co-Mo-S slabs (Figure 1). At the 9th Iberoamerican symposium on catalysis in Lisbon in 1984, Topsøe researchers published results from studies showing that there was a modified Co-Mo-S structure with substantially higher activity per active site than the original Co-Mo-S structure. To differentiate between the two Co-Mo-S structures, these were

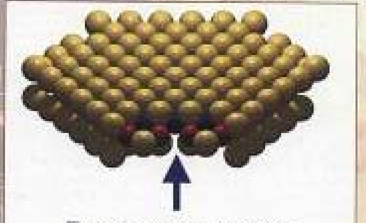


Figure 1. Side view of CoMoS slabs showing type I and II sites.

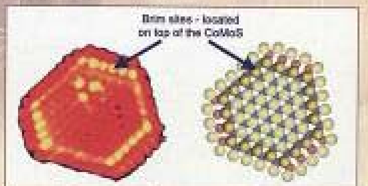
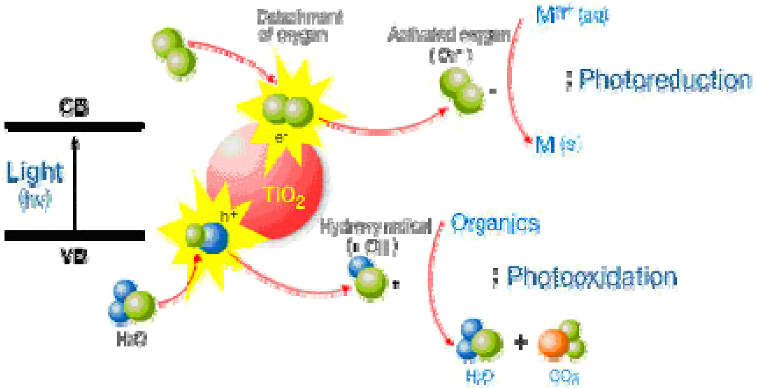
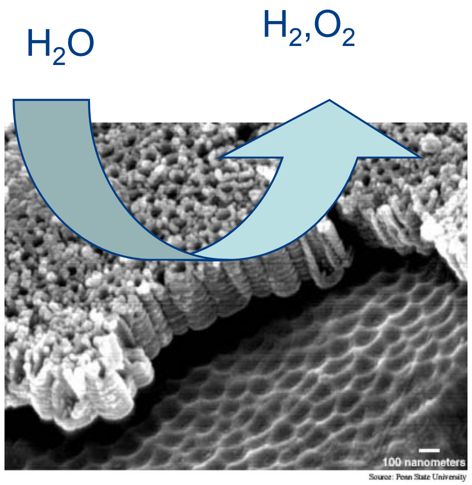


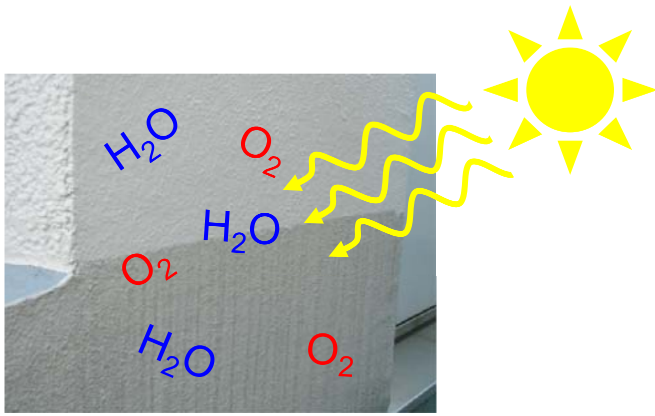
Figure 2. Top view of CoMoS slabs showing brim sites.

Titaniumoxid (TiO_2)

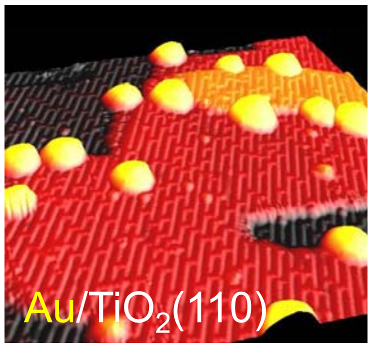
- AOP/disinfection
- Hydrogen production
- Solar cells
- Super-hydrophillic self-cleaning surfaces

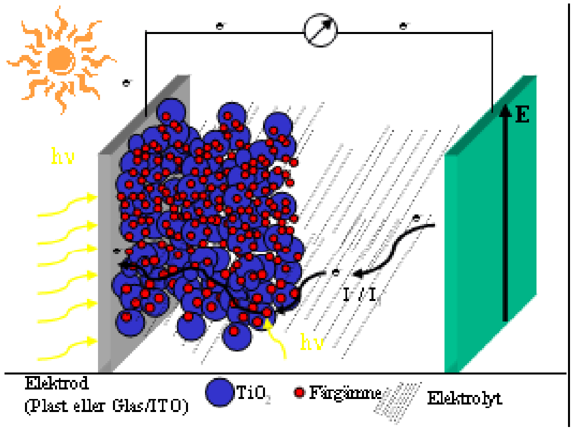






Self-cleaning surface (upper part)

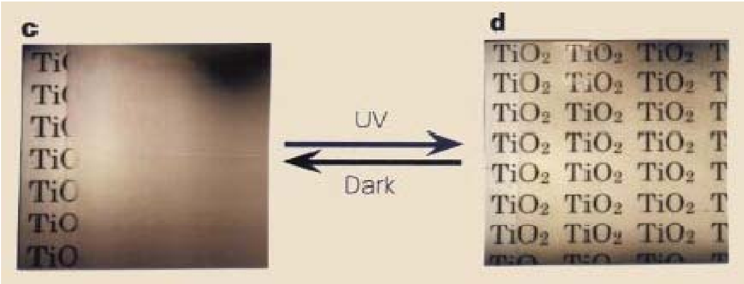




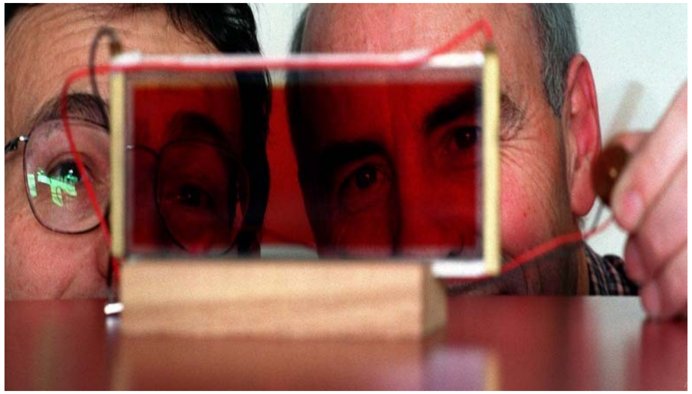
Titaniumdioxide TiO_2

Heterogeneous catalysis

Photocatalysis: water and air purification



Wang et al., Nature **388**, 431 (1997)

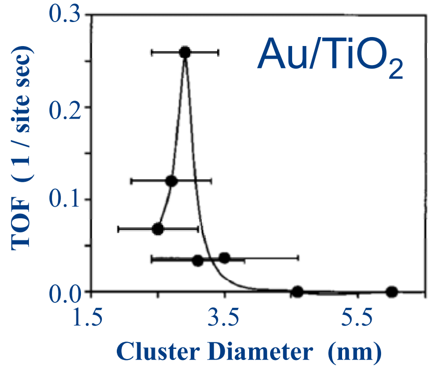


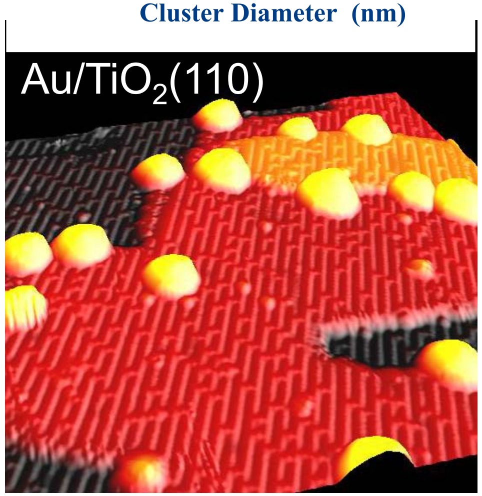
O'Regan et al., Nature **353**, 737 (1991)

$$H_2O \xrightarrow{UV} H_2 + \tfrac{1}{2} O_2$$

Fujishima and Honda, Nature **238**, 37 (1972)

$CO + ½ O_2 \rightarrow CO_2$

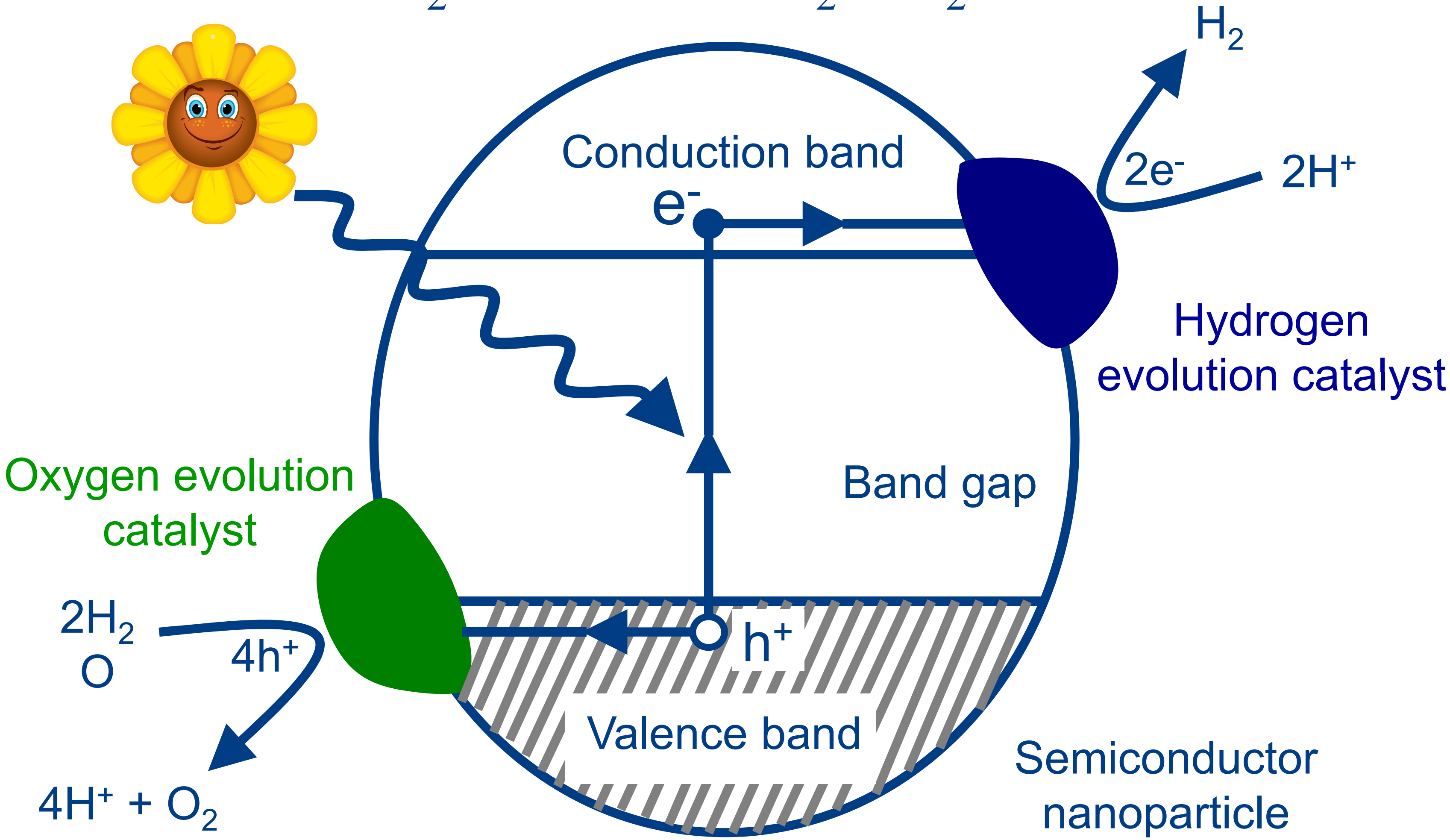




Bamwenda *et al*. Catal. Lett. **44**, 83 (1997),
Haruta *et al*., J. Catal. **115**, 301 (1989),
Valden *et al*., Science **281**, 1648 (1998).
U. Diebold, Surf. Sci. Rep. **48**, 53 (2003).

Photo-electrochemical water splitting

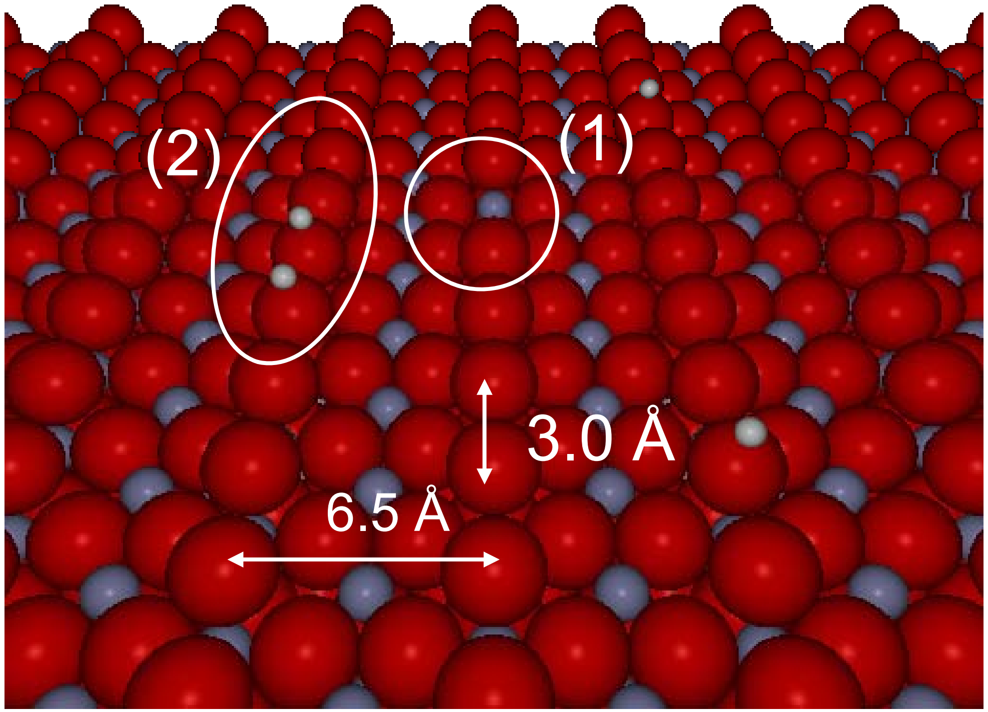
$$H_2O + h\nu \rightarrow \frac{1}{2}O_2 + H_2$$

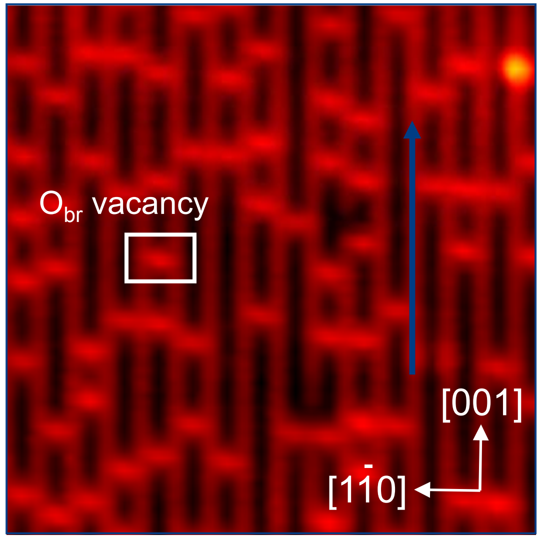


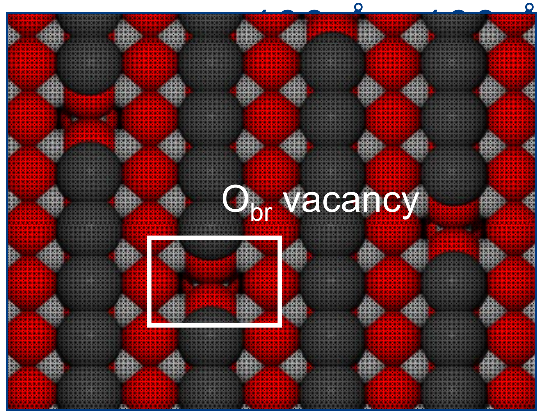
Linsebigler, Lu, Yates, Chem. Rev. **95**, 735 (1995) , Grätzel, Lewis, Domen, Li ….

The structure of the rutile $TiO_2(110)$ surface

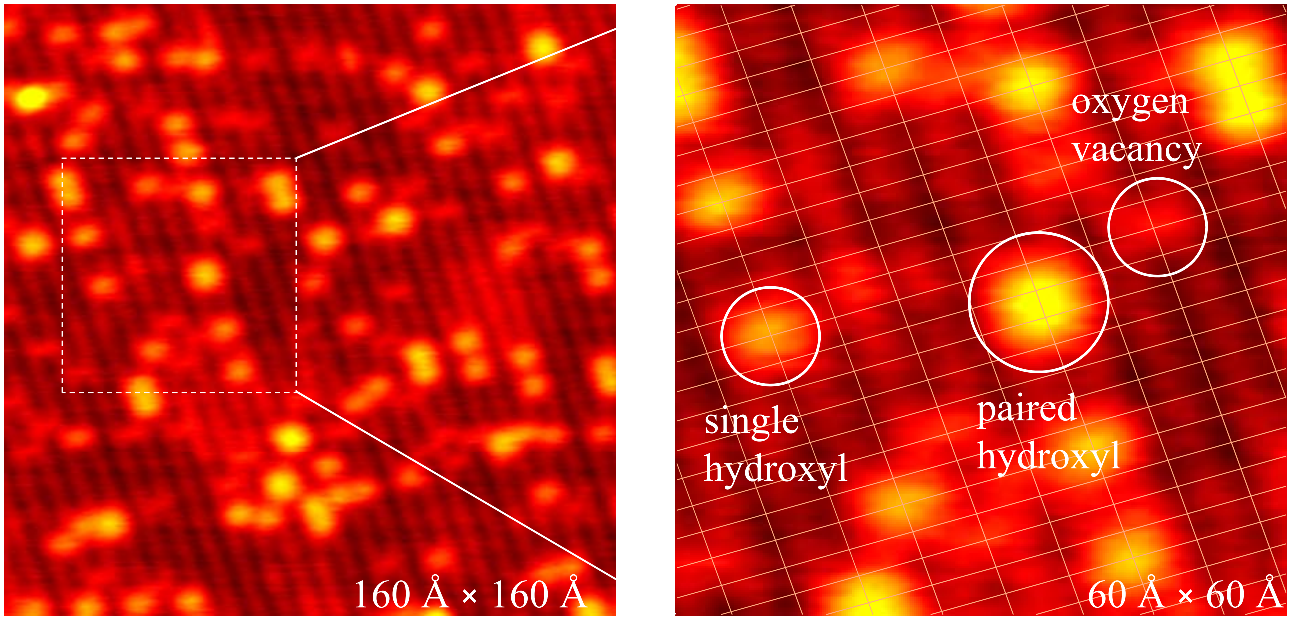
- Ar^+ sputtering @ RT
- Annealing to 823-973 K in vacuum

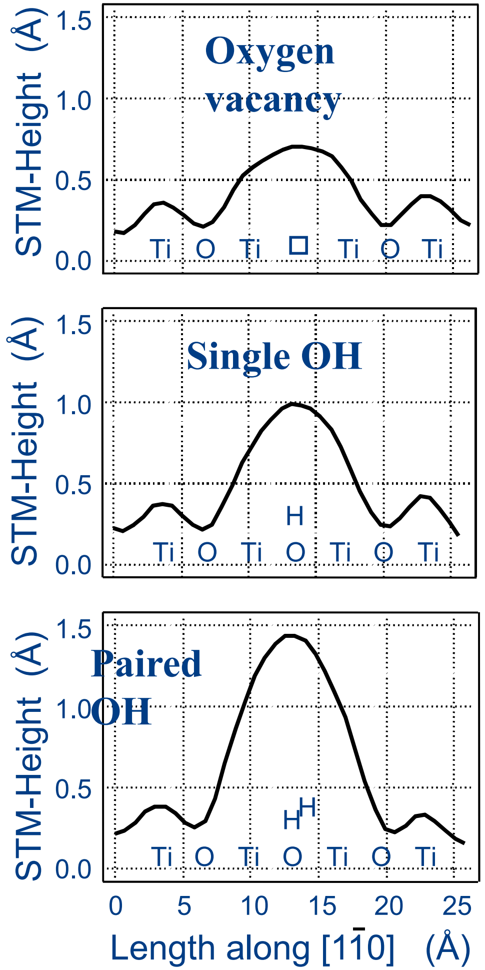






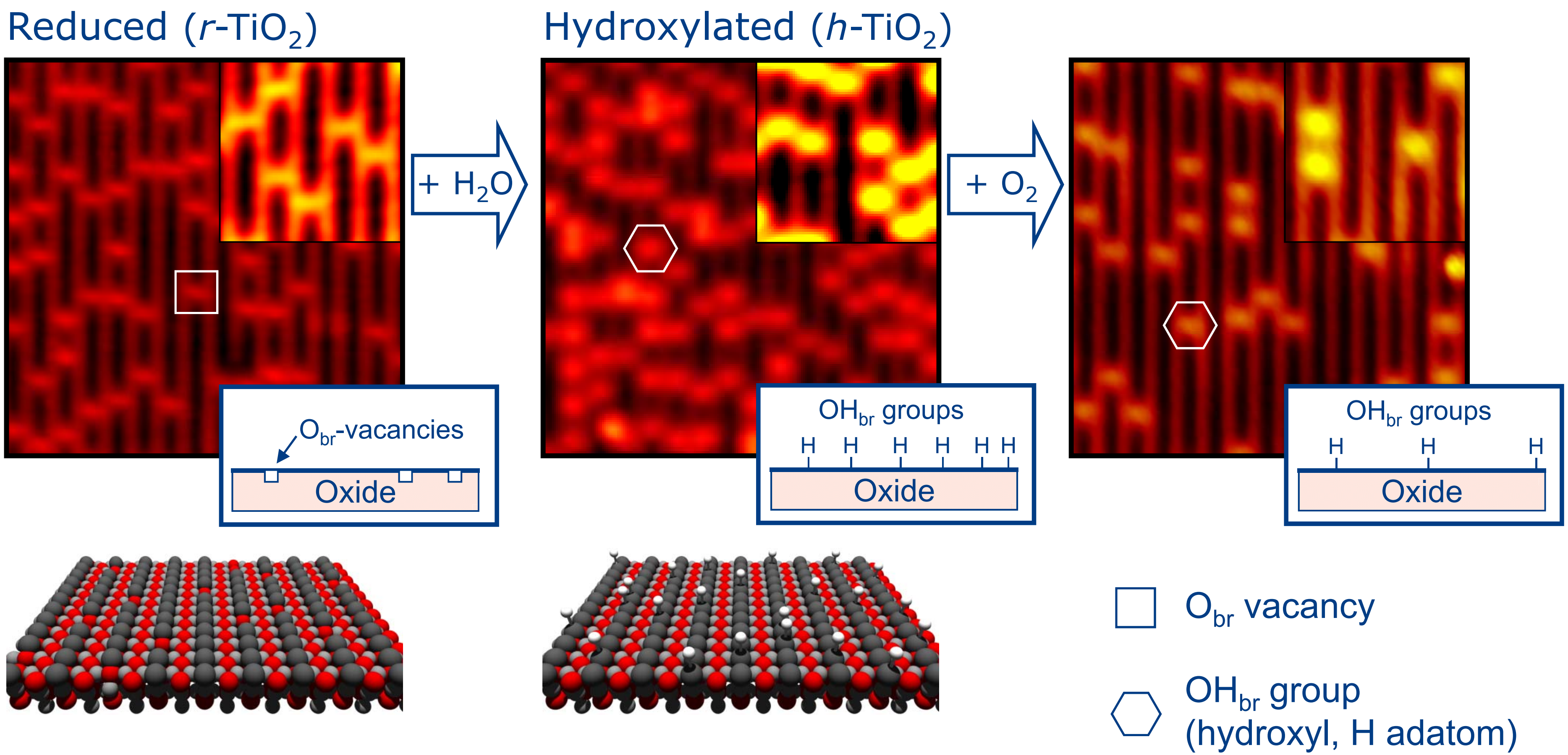
The different defects observed by STM



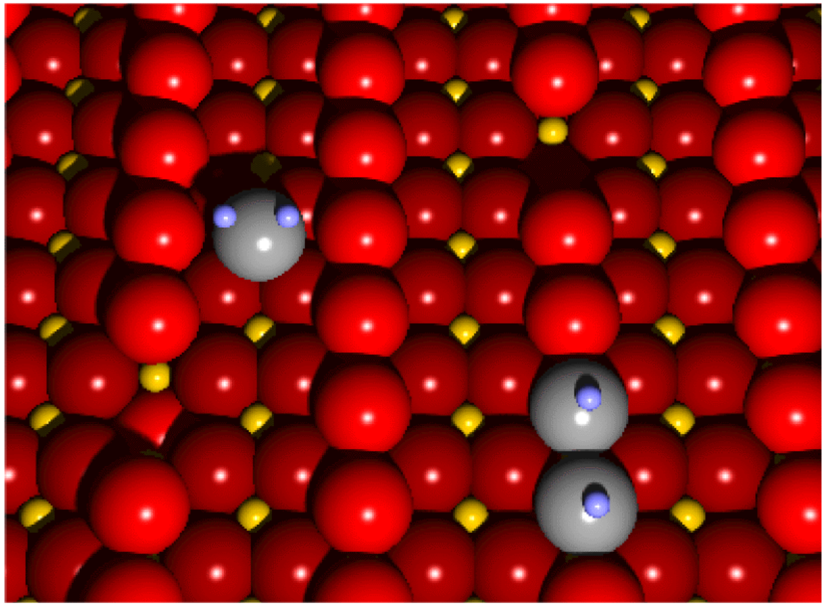


S. Wendt et al PRL **96**, 066107

Preparation of hydroxylated $TiO_2(110)$



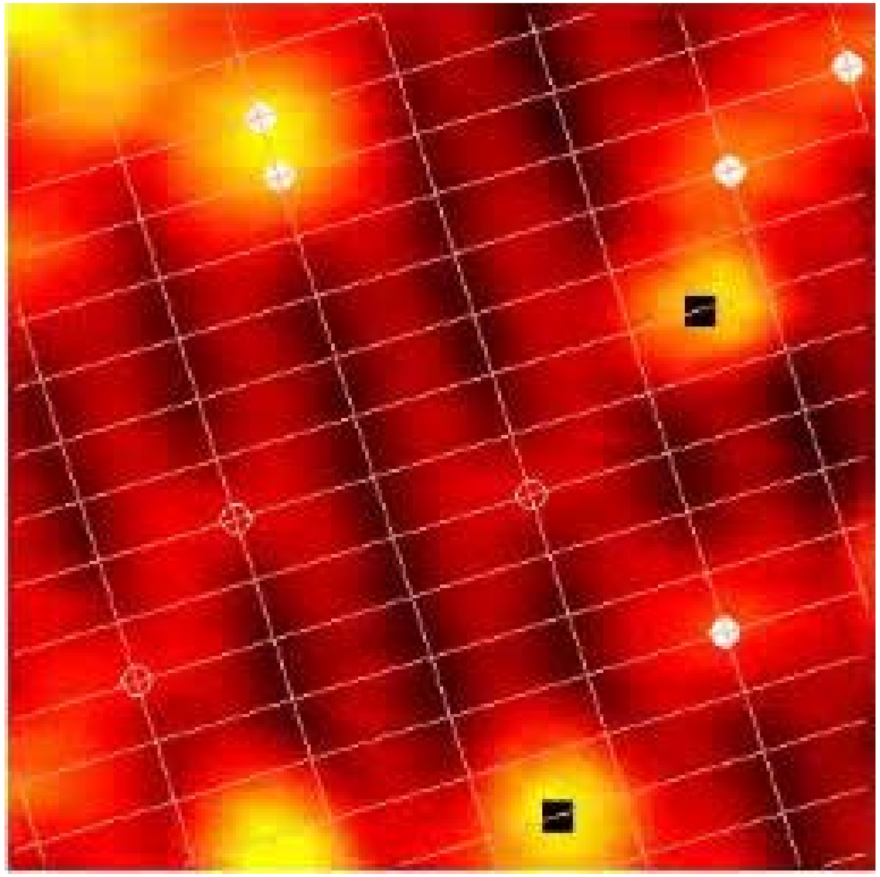
H_2O dissociation on $TiO_2(110)$



- $TiO_2(110)$ surface with O_{br} vacancies
- Adsorption of H_2O molecules from the gas phase
- H_2O molecules diffuse along the 5f-Ti rows
- H_2O molecules fill O_{br} vacancies
- Proton transfer reaction along the O_{br} row.

Oxygen vacancies are active sites for Water dissociation

Dissociation of Water monomers on TiO_2(110)

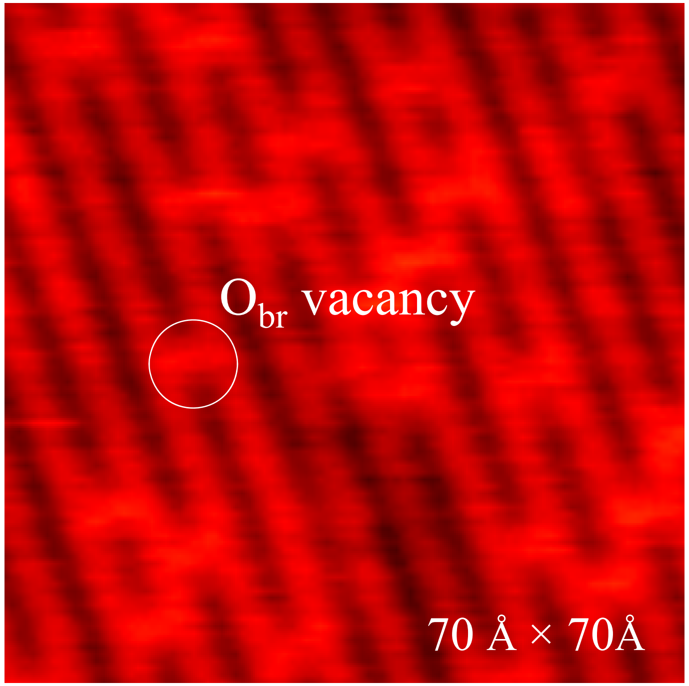


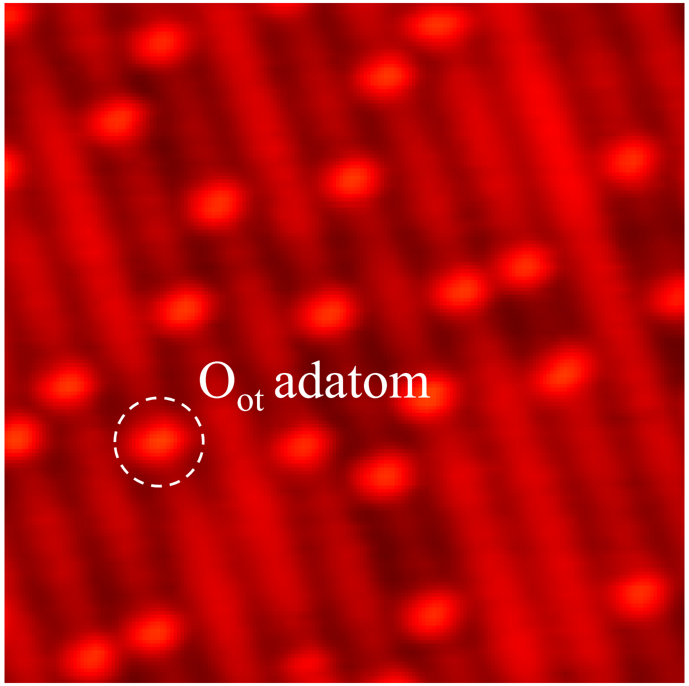
187 K

S. Wendt et al Surf. Sci. 598, 226 and PRL 96, 066107
Matthey, Wendt, Hammer, Besenbacher, Science 315, 1692 (2007)
Wendt, …Hammer, F. Besenbacher, Science 320, 1755 (2008)

O_2 dissociation

5.5 %ML O_{br} vac.

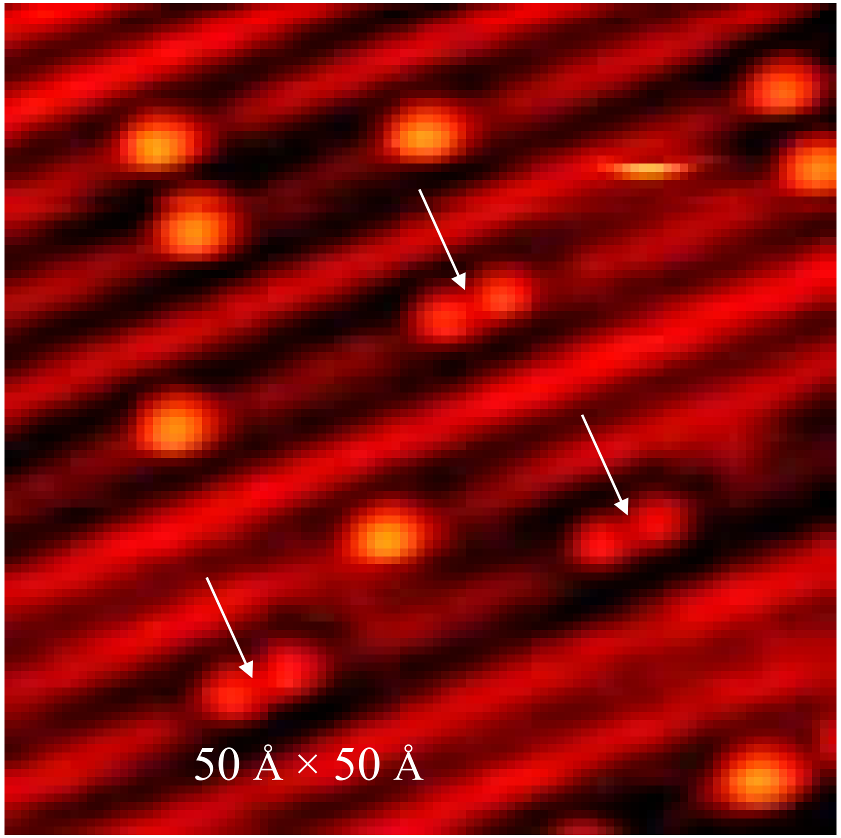




S. Wendt et al Surf. Sci. 598, 226 and PRL 96, 066107
Matthey, Wendt, Hammer, Besenbacher, Science 315, 1692 (2007)

New O_2 dissociation channel in the Ti trough

r-TiO_2(110):
8 %ML O_{br} vac.

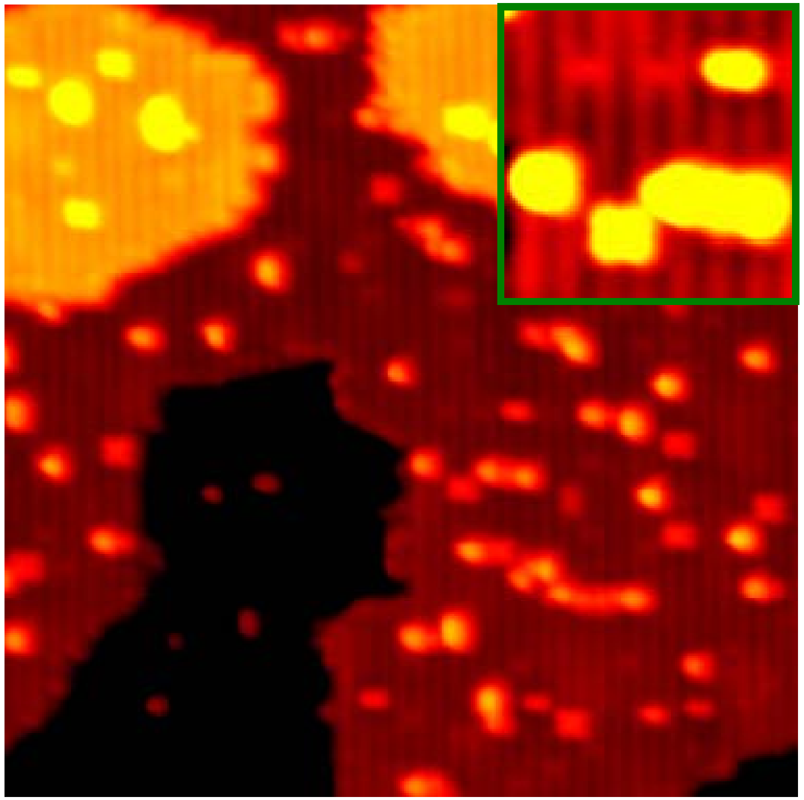


6 L O_2 at 127 K + flash to 266 K

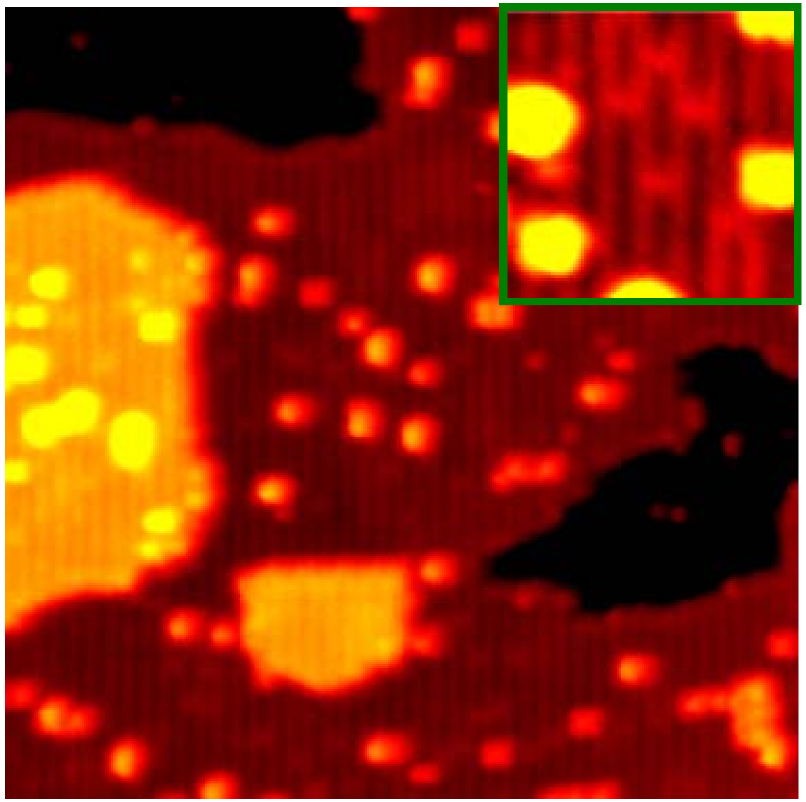
pairs of nearest-neighbor O_{ot} adatoms

S. Wendt, …Bjørk Hammer, F. Besenbacher, Science 320, 1755 (2008)

Ti diffusion toward the surface and: Formation of new TiO_x ad-structures



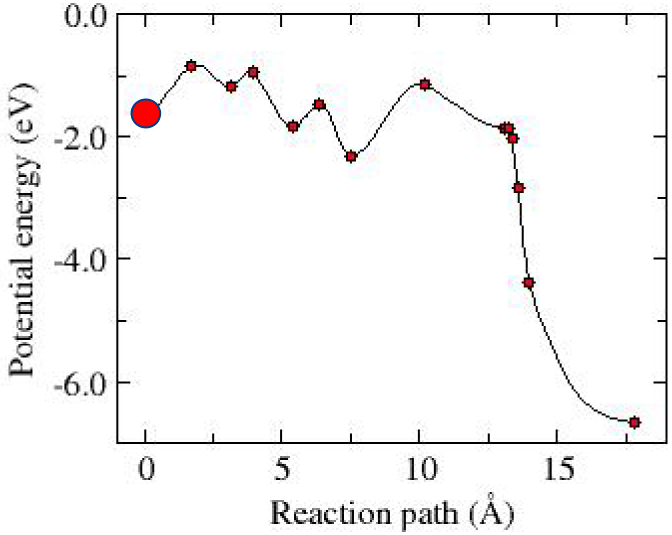
heated to 595 K

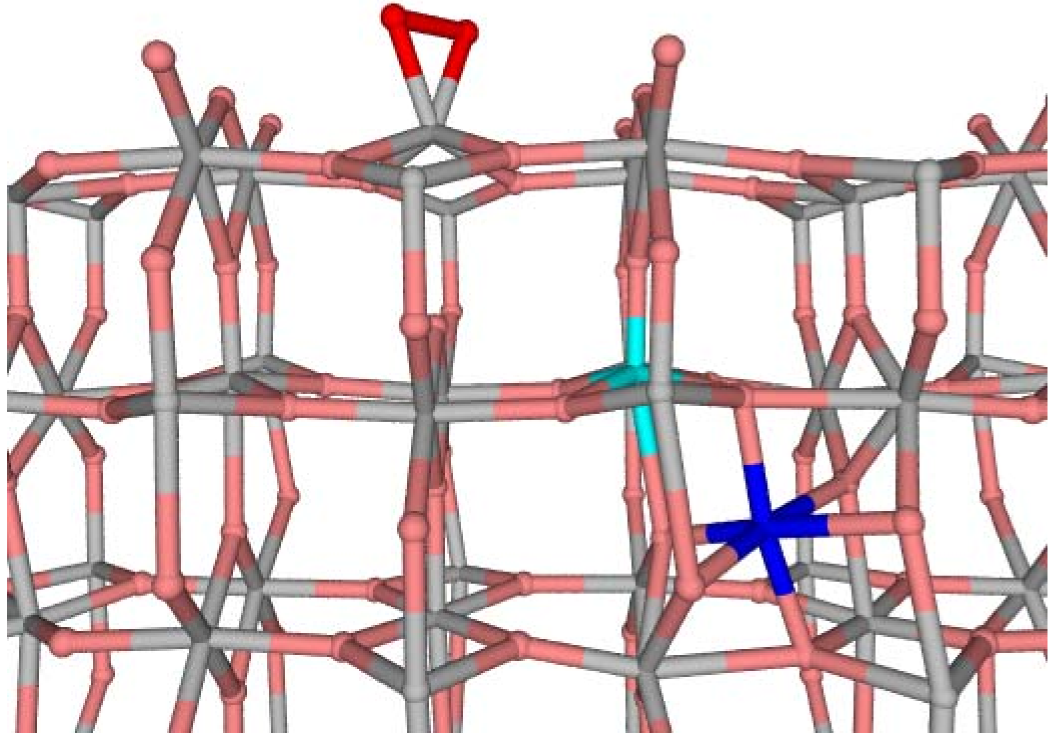


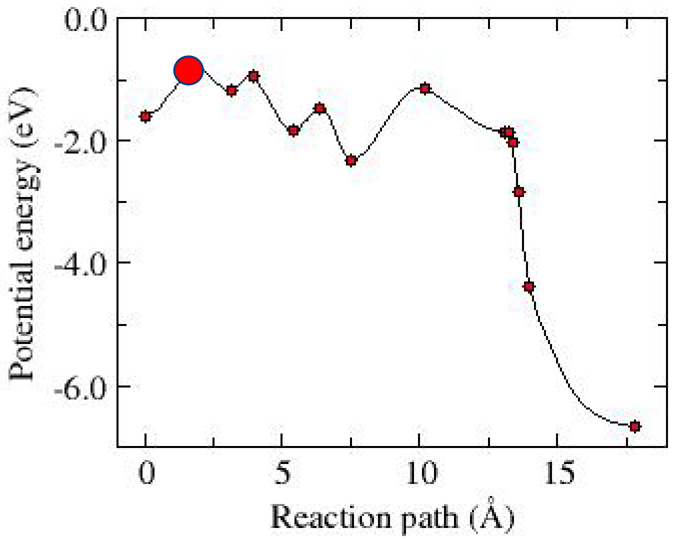
heated to 698 K

S. Wendt, …Bjørk Hammer, F. Besenbacher, Science 320, 1755 (2008)

Ti diffusion toward the surface and: Formation of new TiO_x ad-structures







0.0
-2.0
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-6.0
Potential energy (eV)
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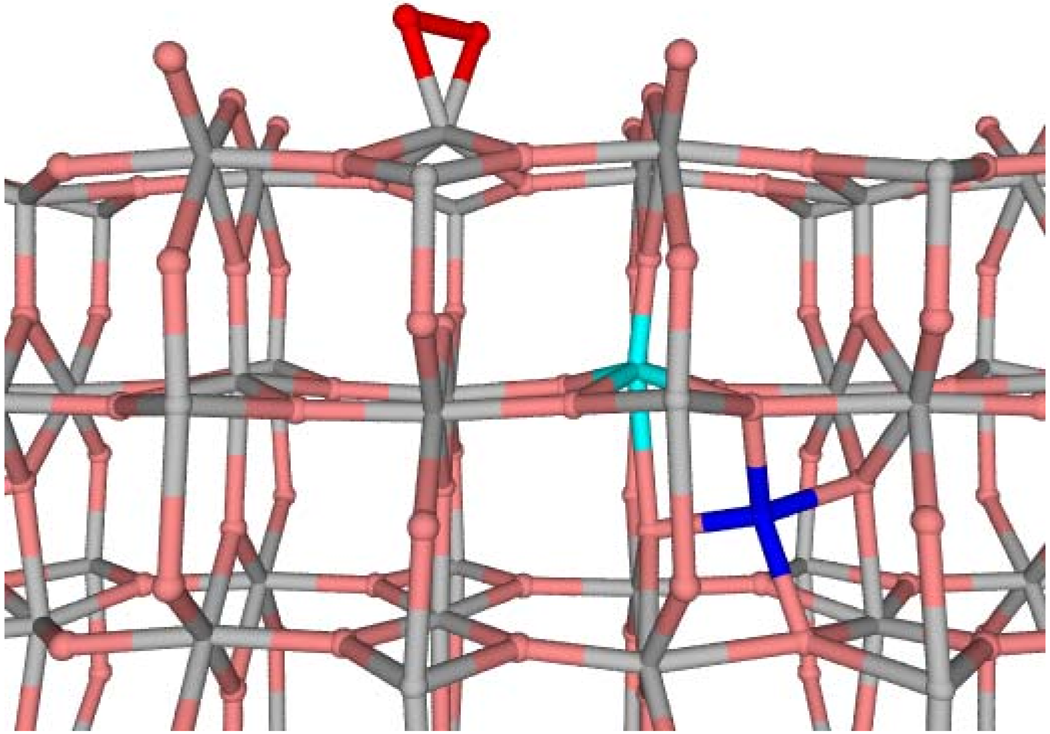
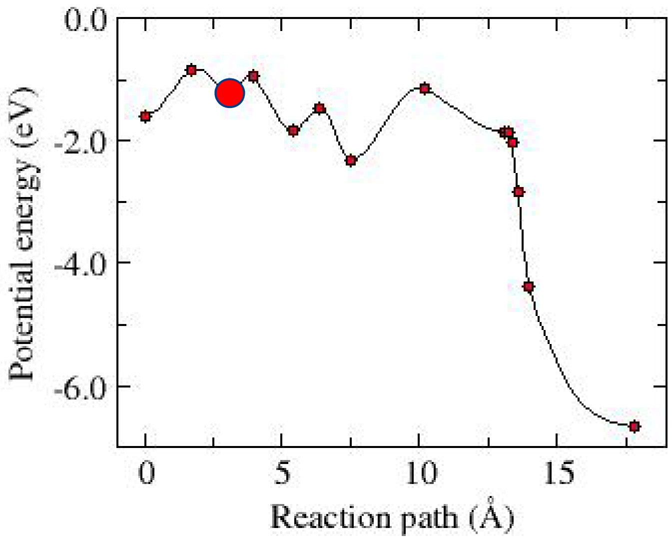
5
10
15
Reaction path (Å)

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-6.0
Potential energy (eV)
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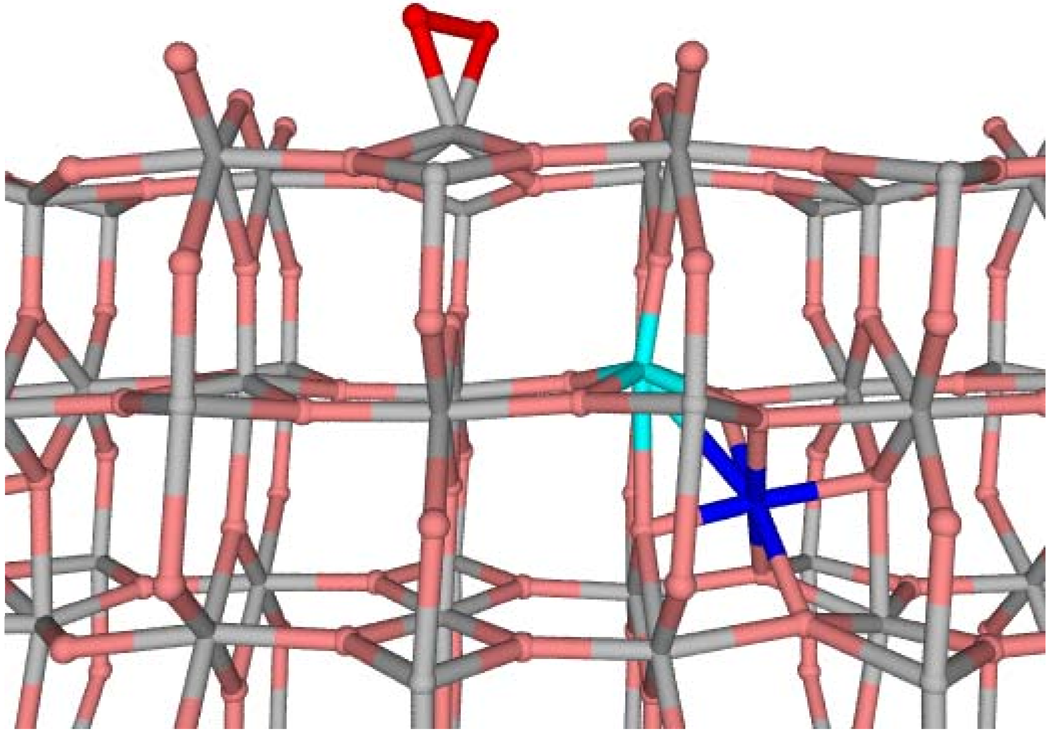
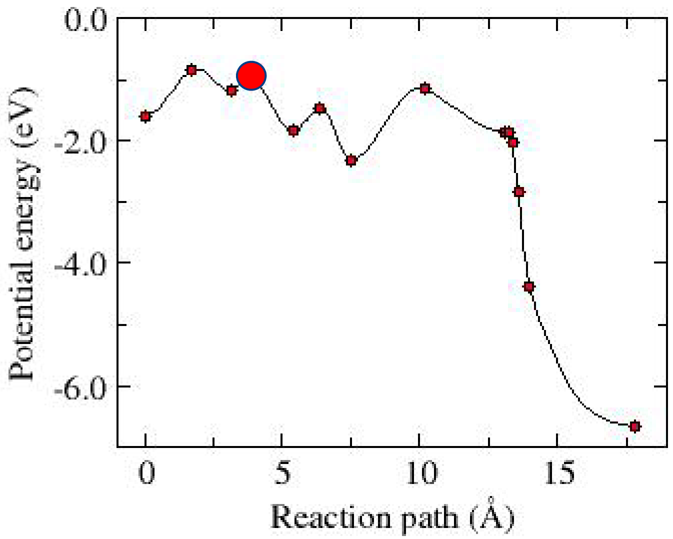
Reaction path (Å)

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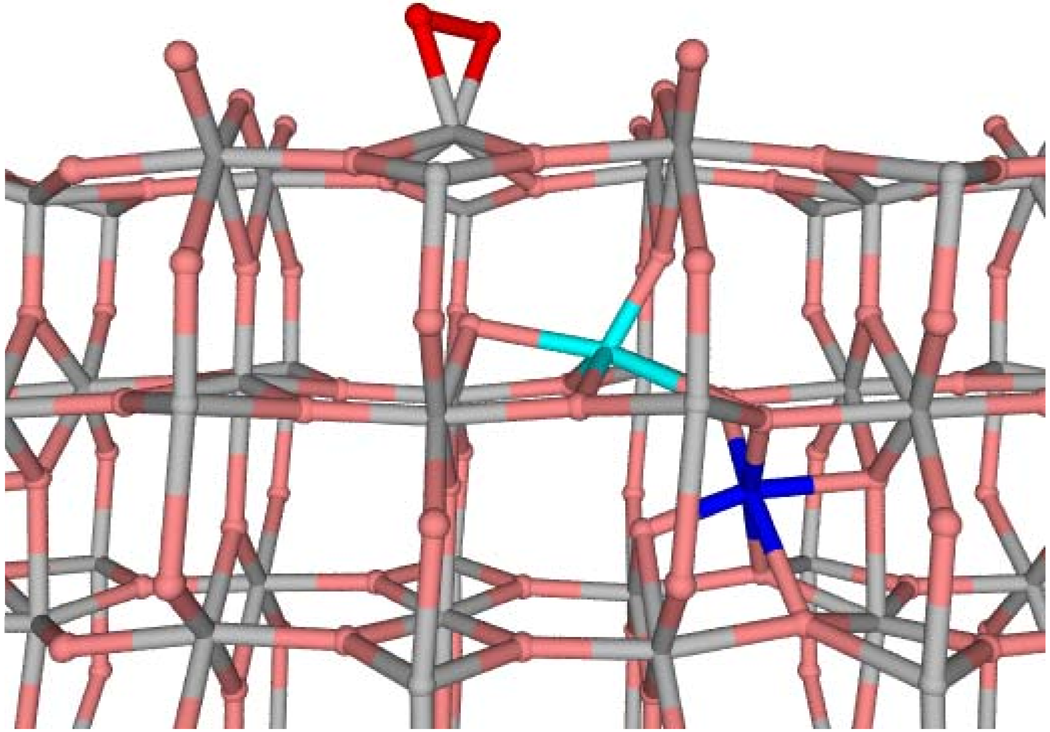

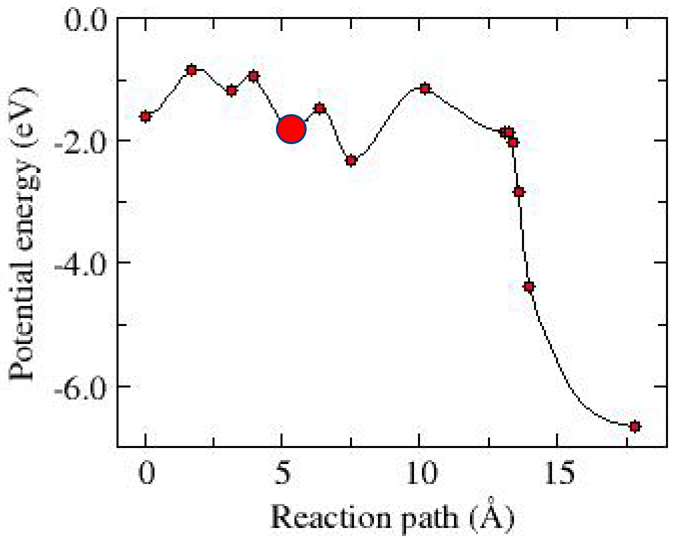
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Potential energy (eV)
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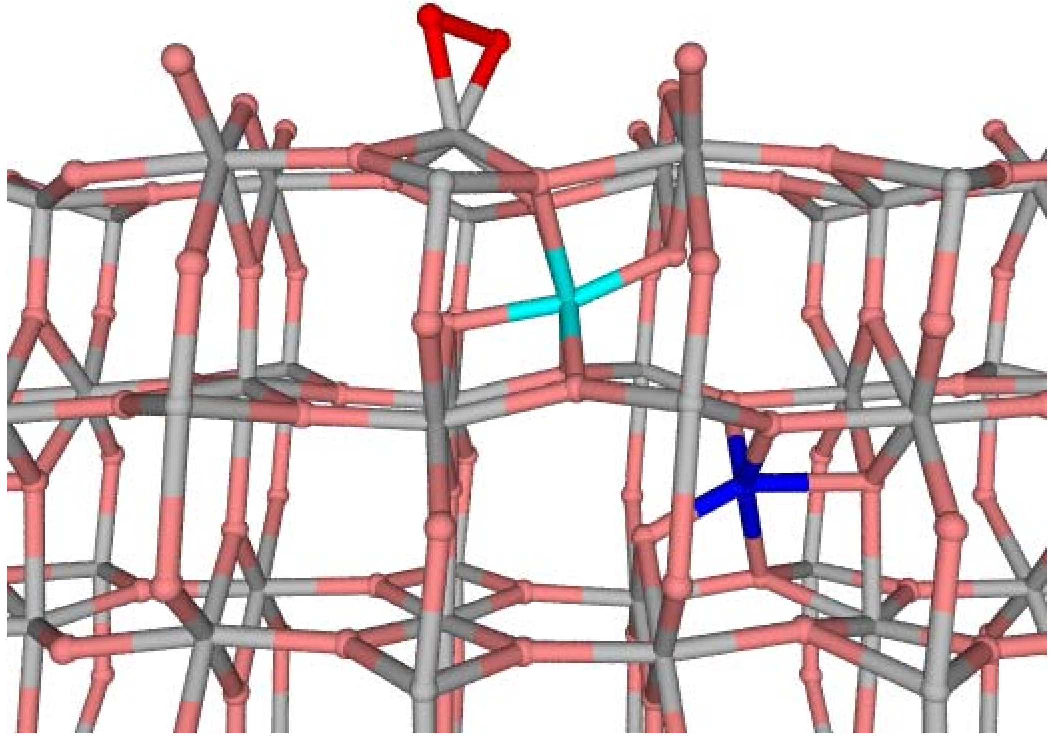
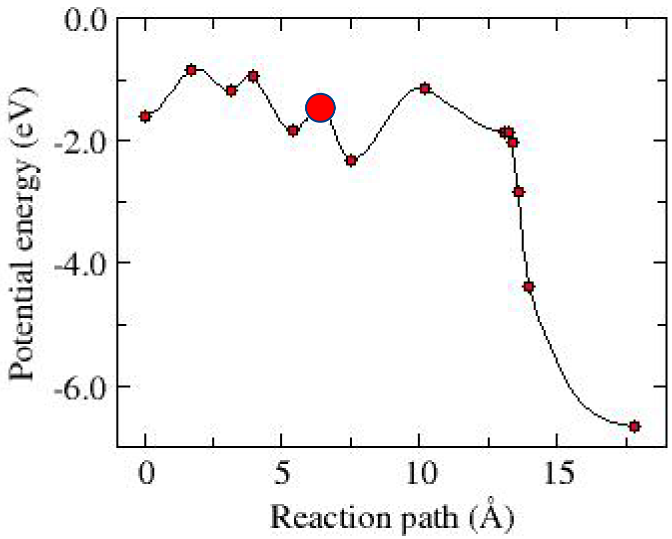
Reaction path (Å)

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-6.0
Potential energy (eV)
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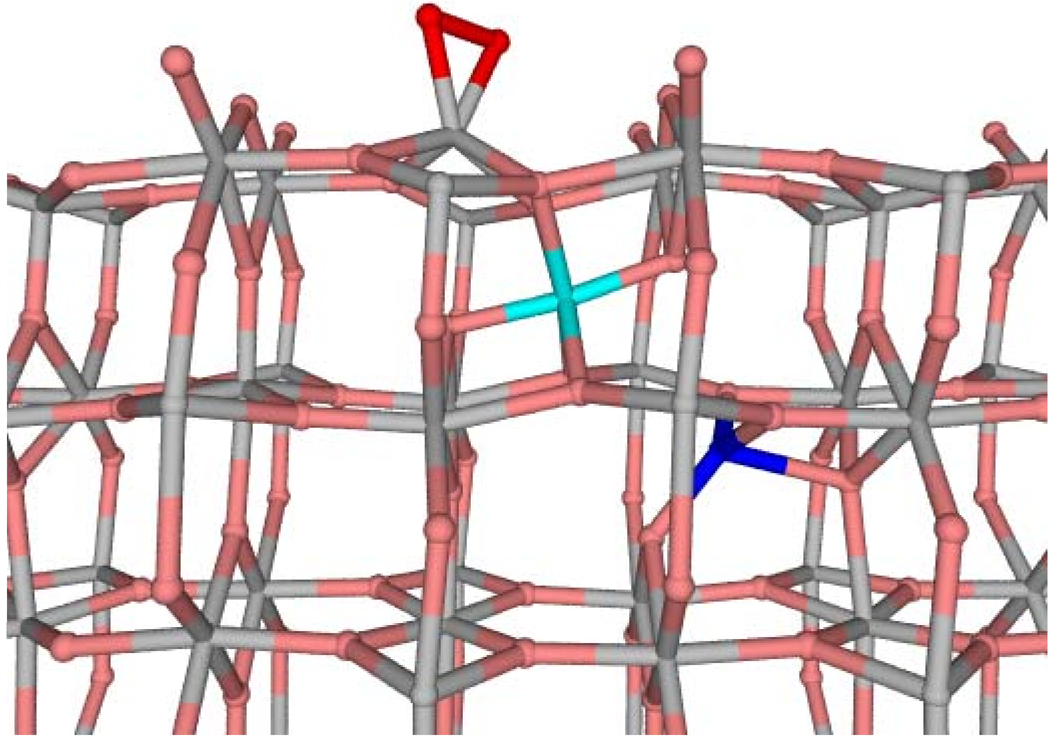
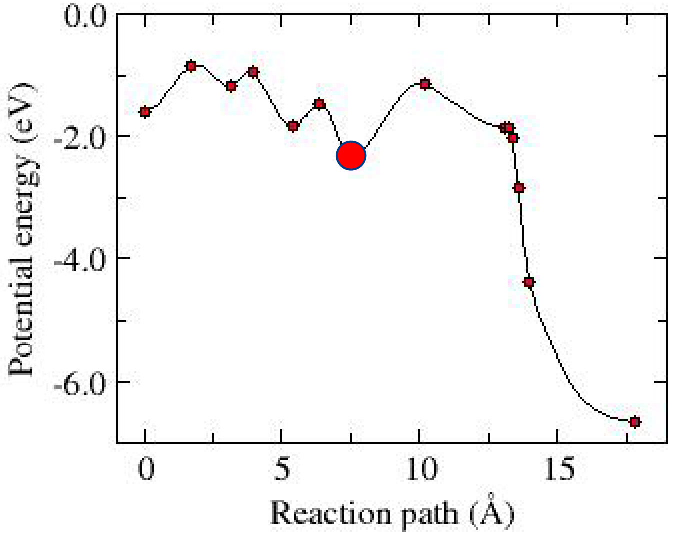
Reaction path (Å)

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-6.0
Potential energy (eV)
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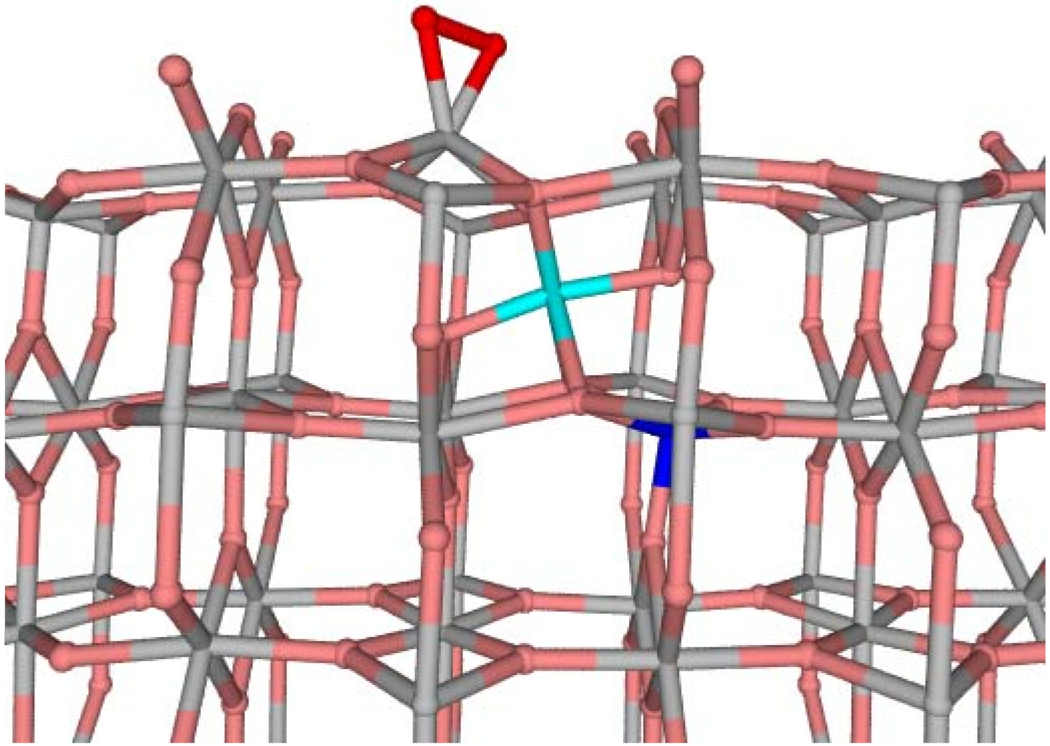
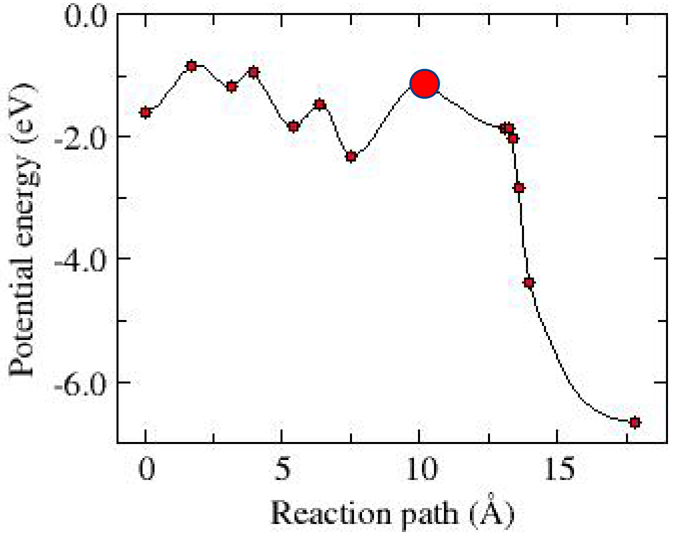
Reaction path (Å)

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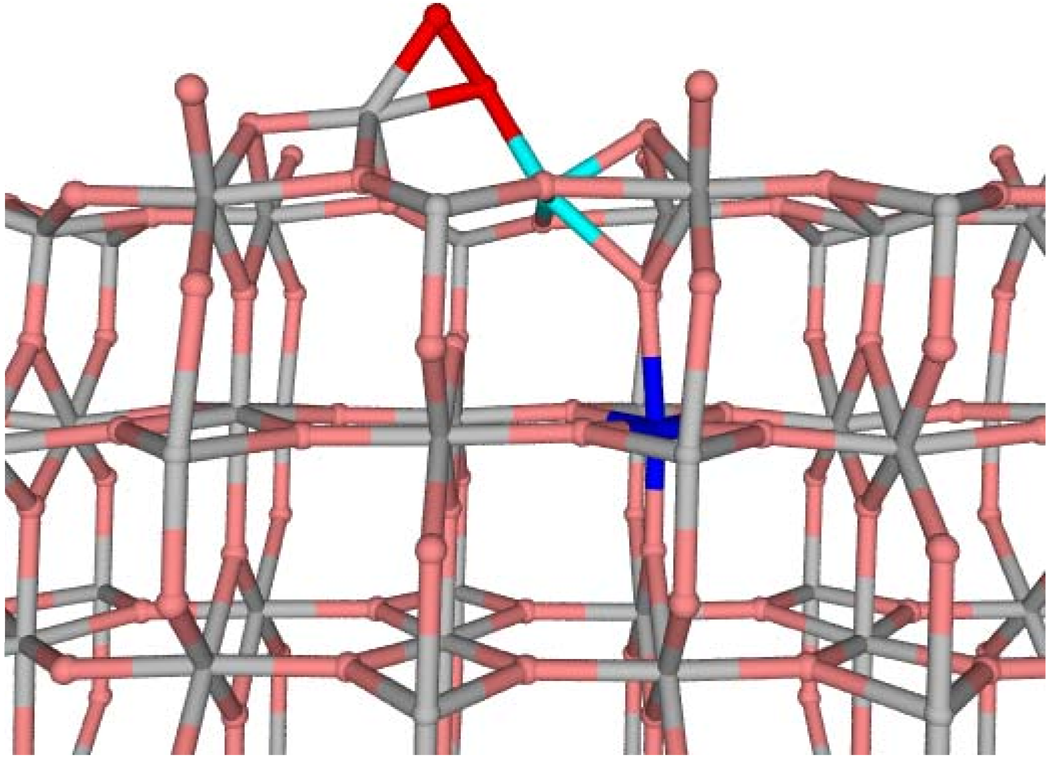
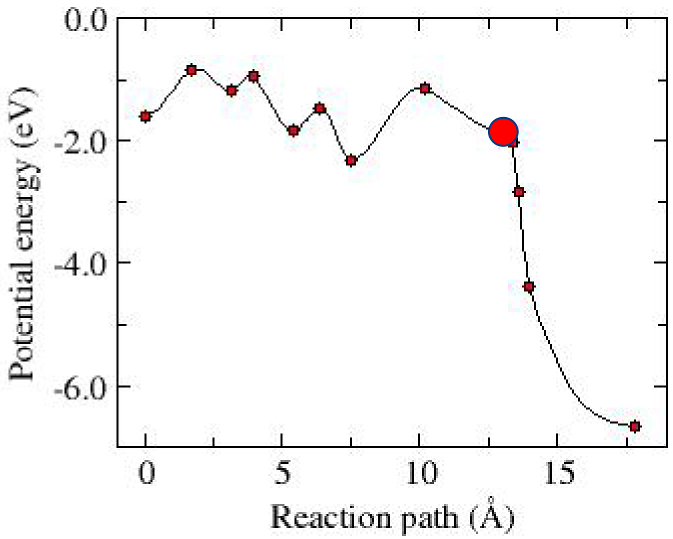
Potential energy (eV)
0
5
10
15
Reaction path (Å)

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Potential energy (eV)
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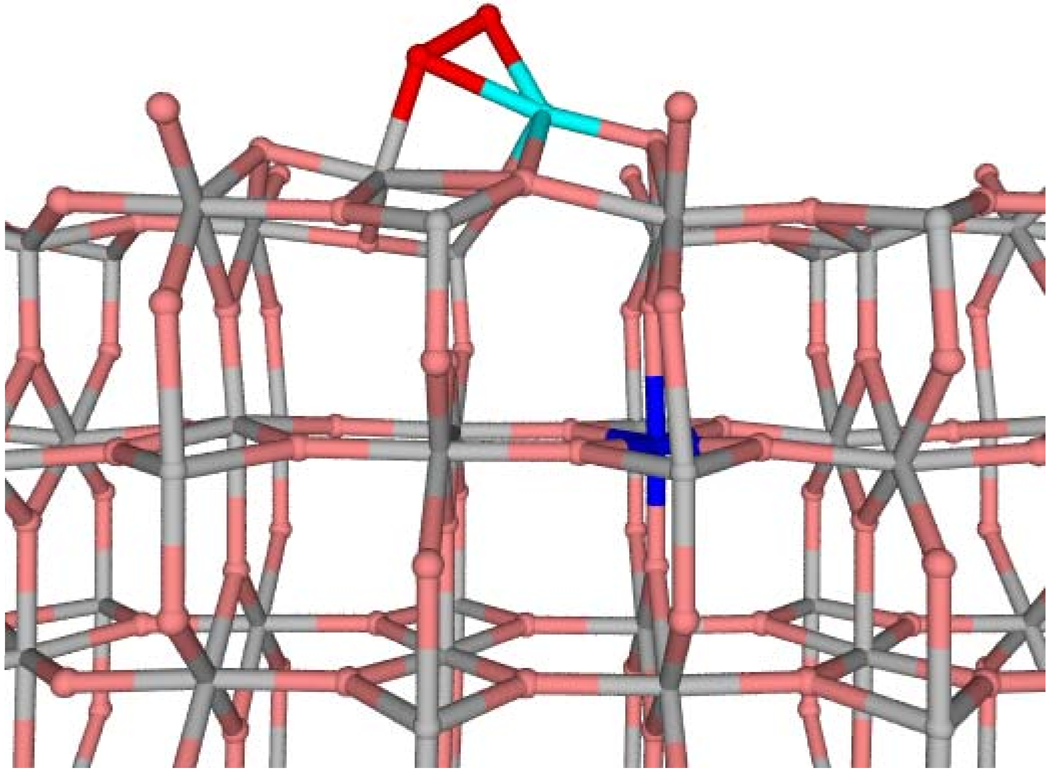
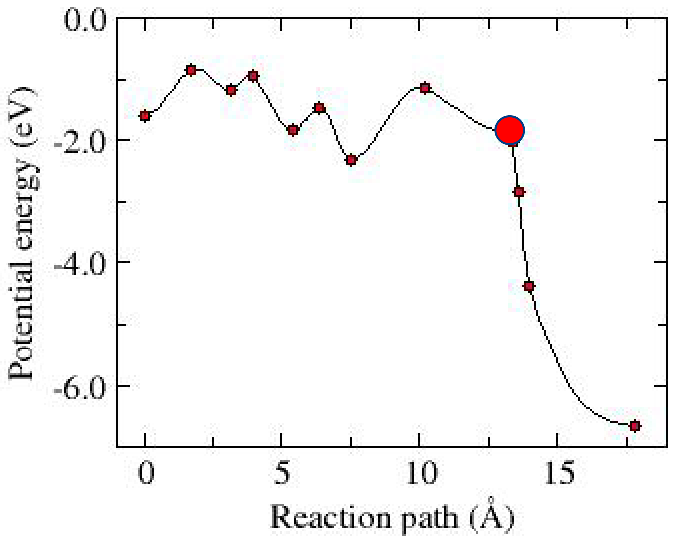
Reaction path (Å)

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Potential energy (eV)
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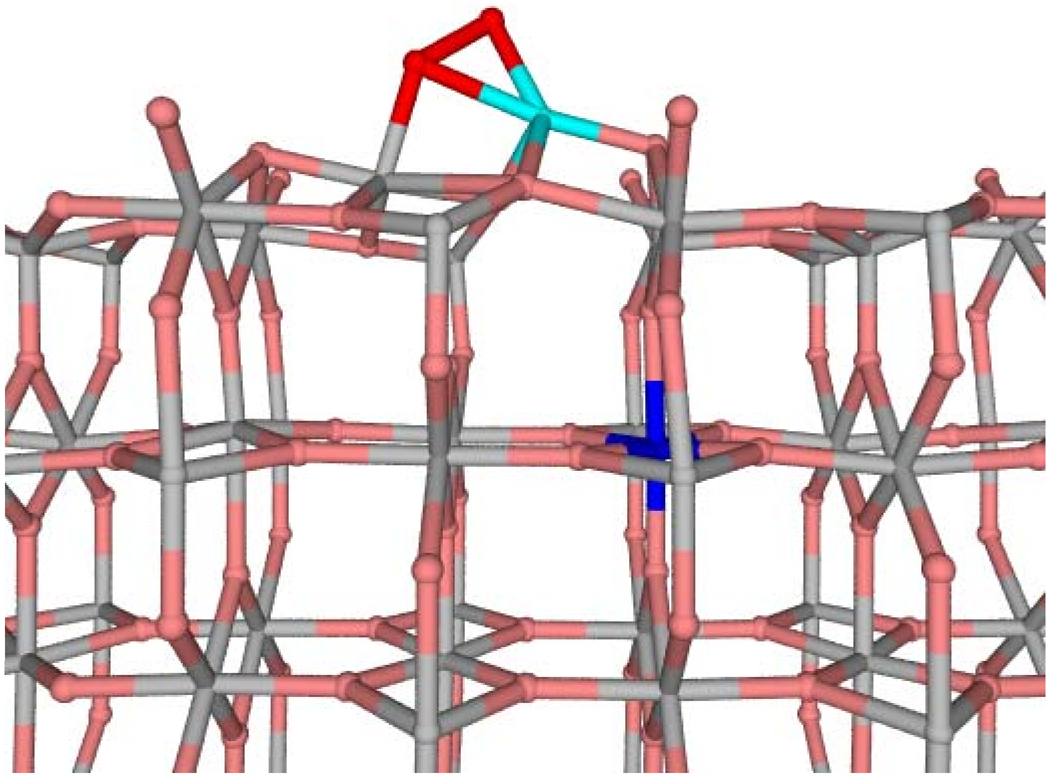
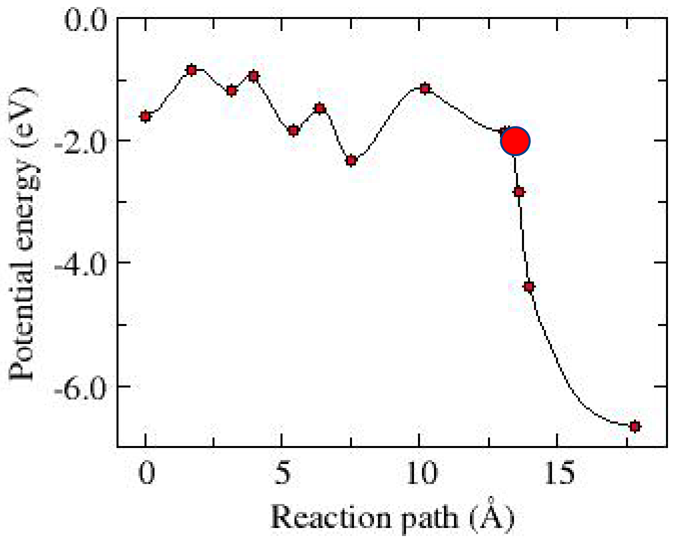
Reaction path (Å)





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Potential energy (eV)
0
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10
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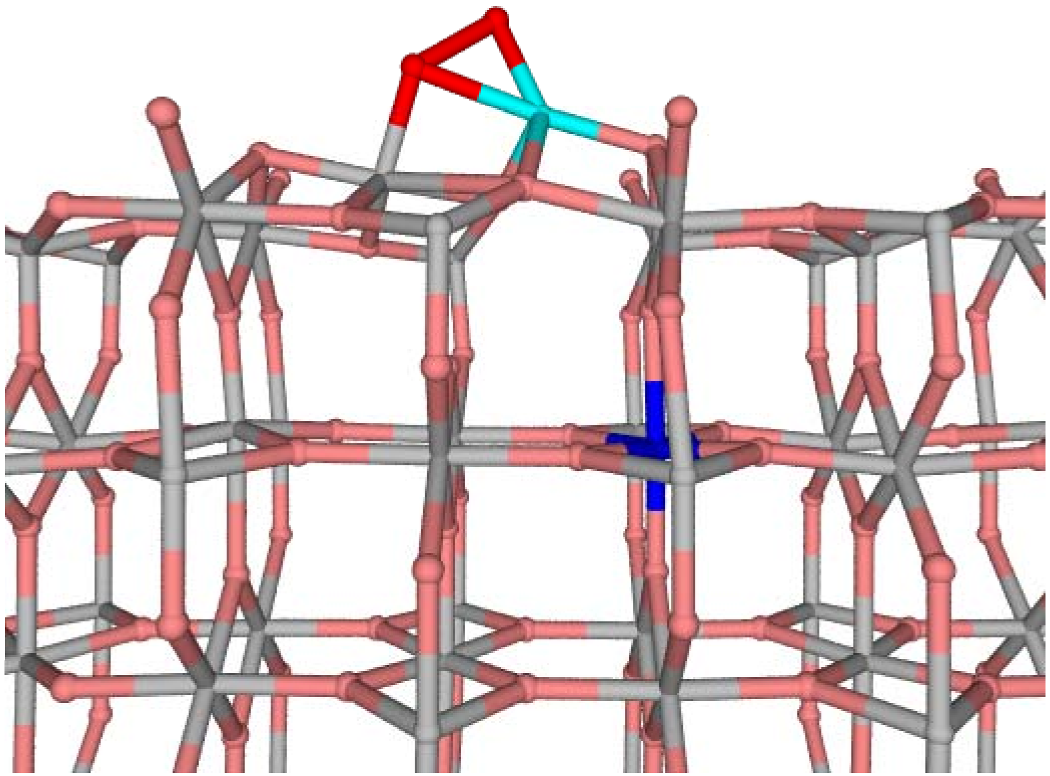
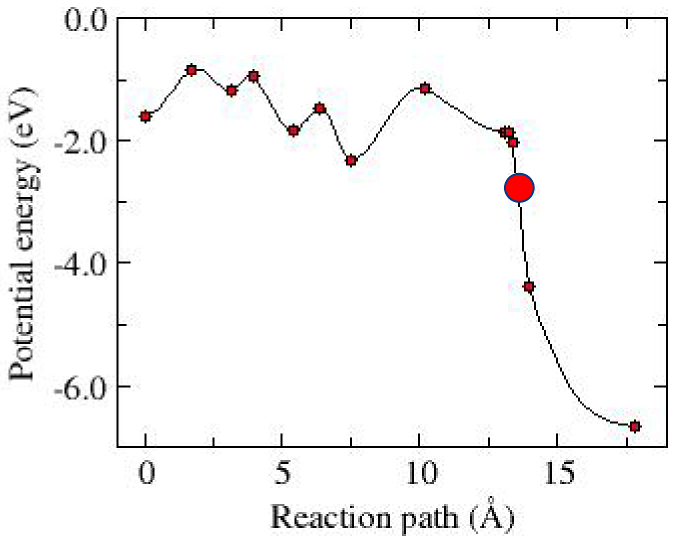
Reaction path (Å)

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Potential energy (eV)
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10
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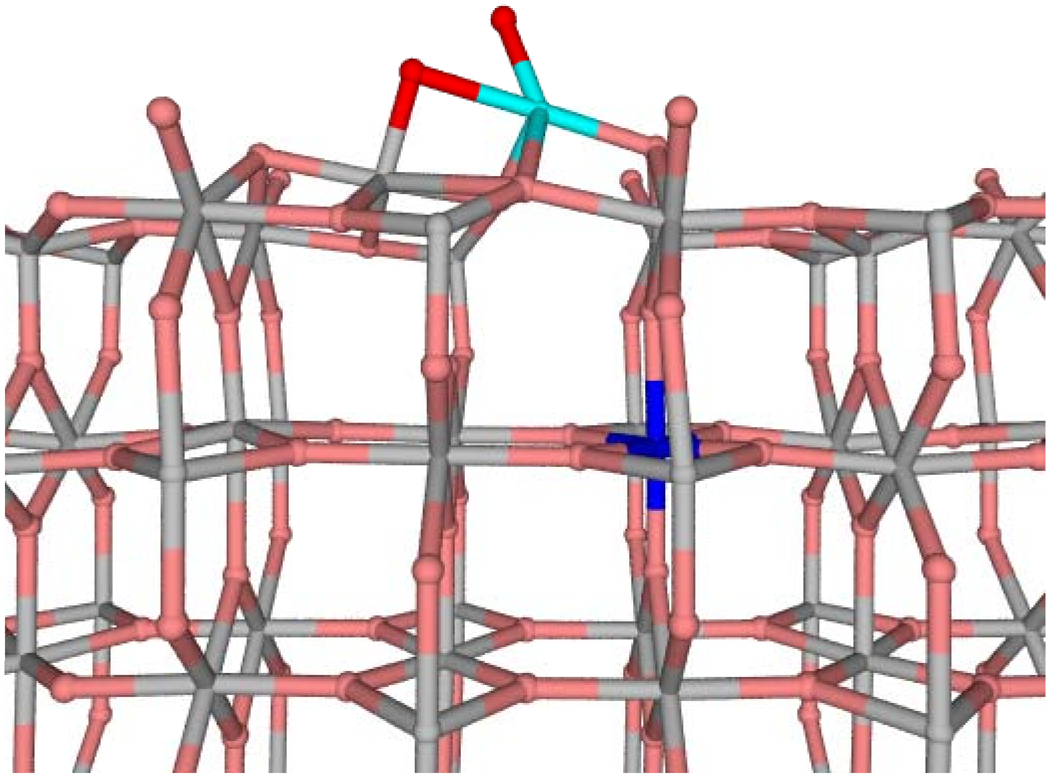
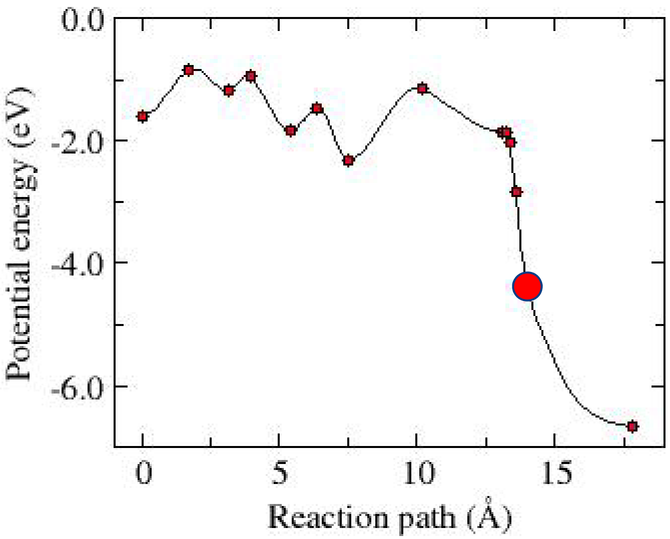
Reaction path (Å)

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Potential energy (eV)
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10
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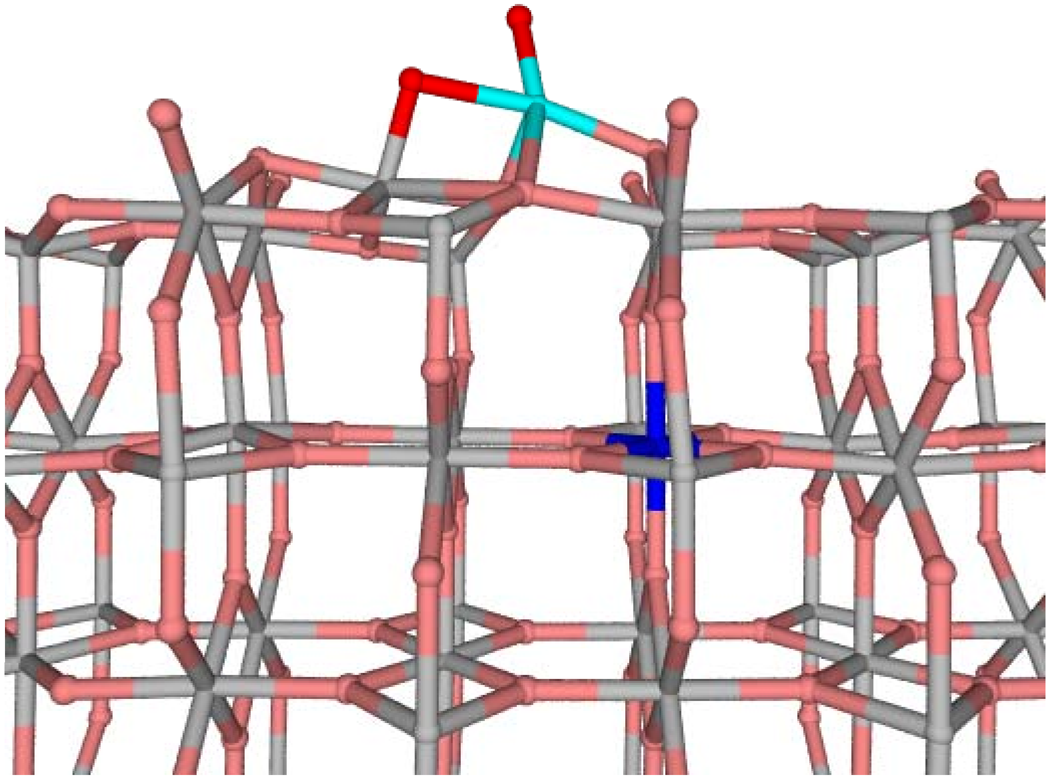
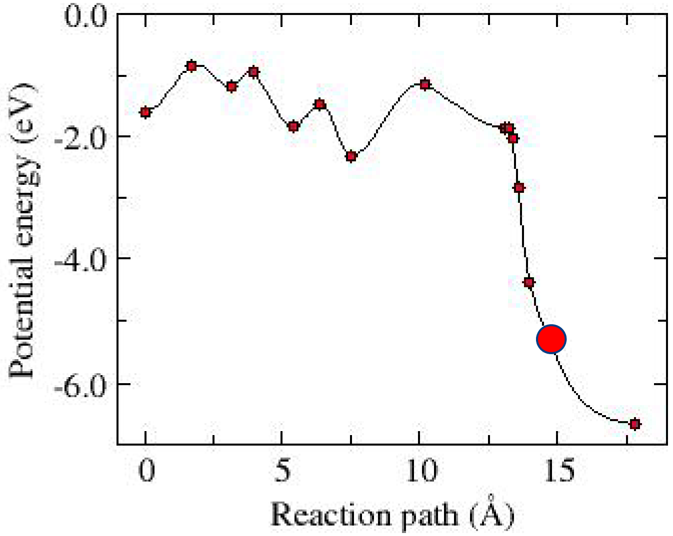
Reaction path (Å)





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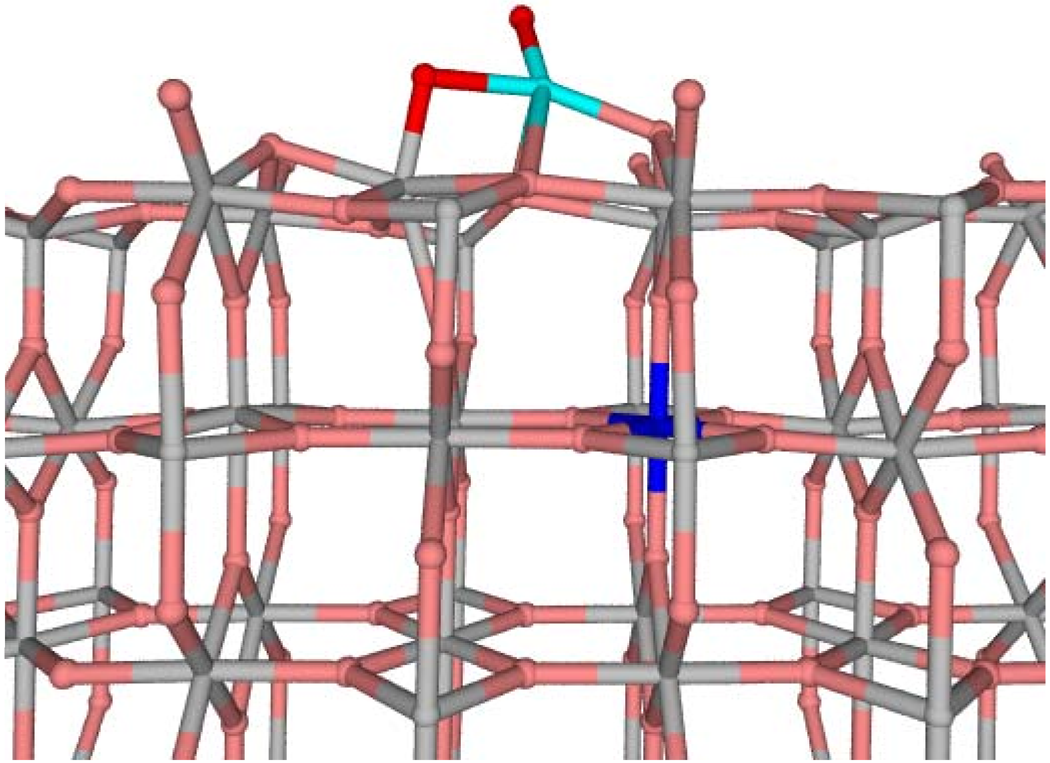
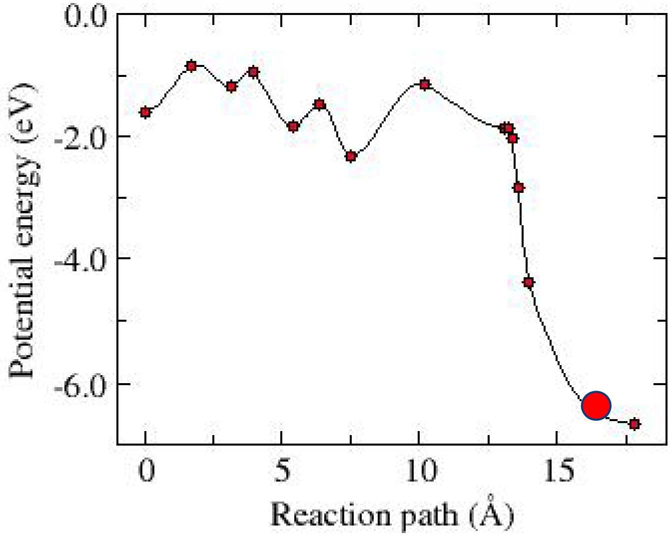
Potential energy (eV)
0
5
10
15
Reaction path (Å)

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Potential energy (eV)
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10
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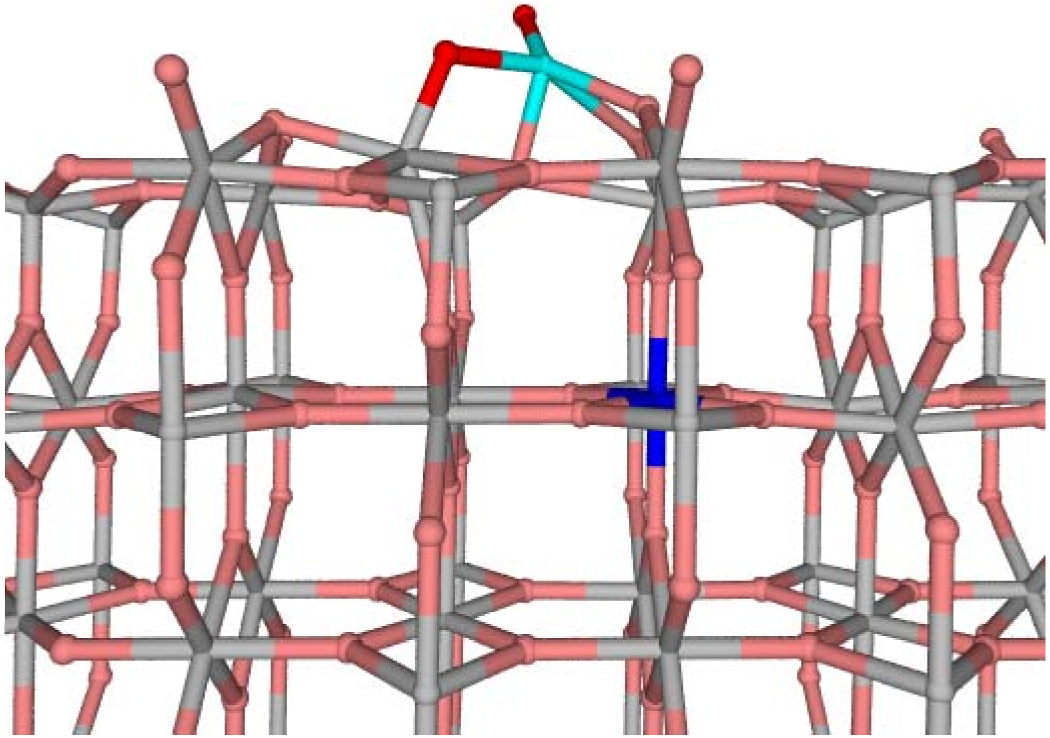
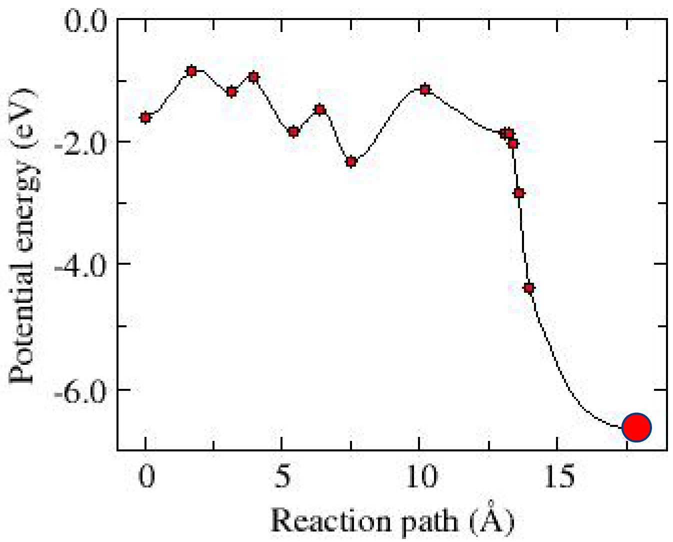
Reaction path (Å)

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Potential energy (eV)
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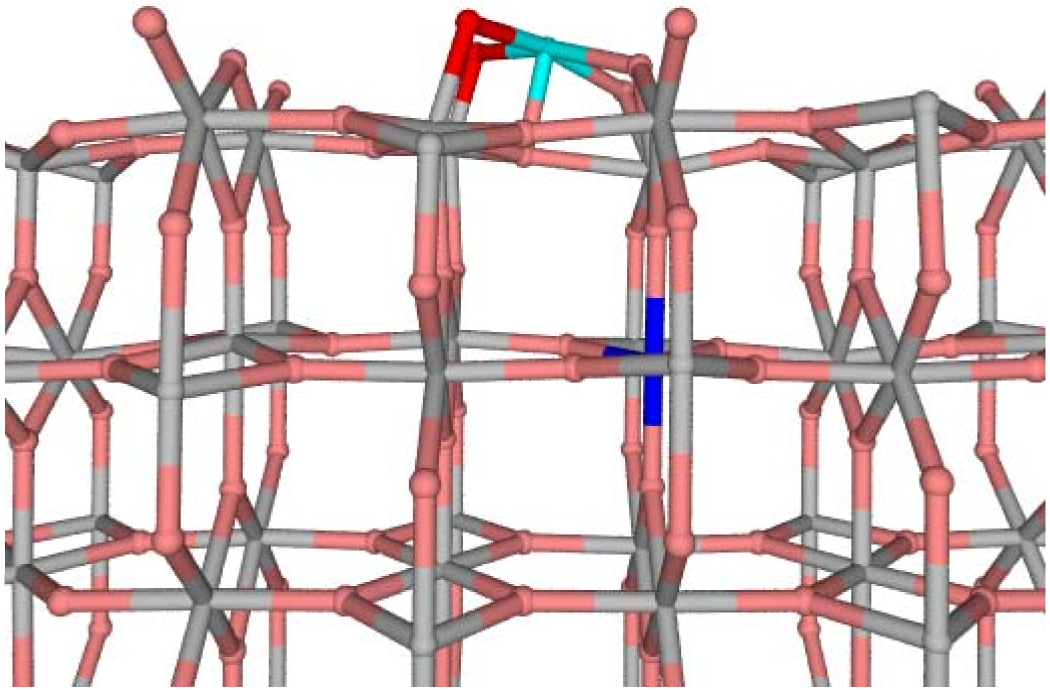
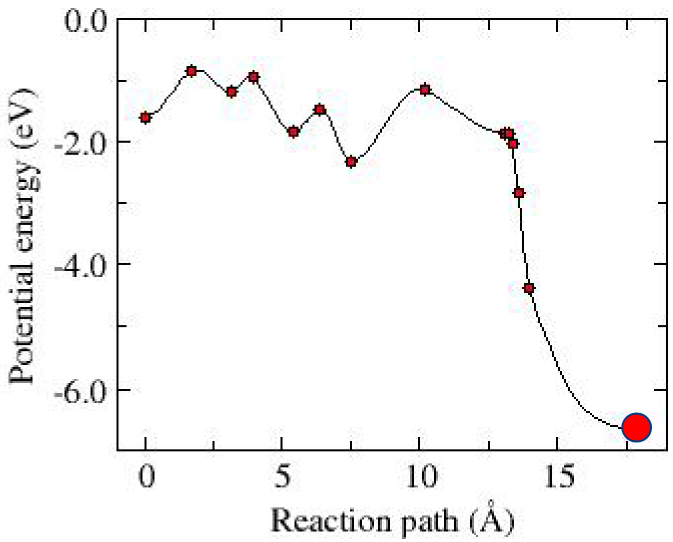
10
15
Reaction path (Å)

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Potential energy (eV)
0
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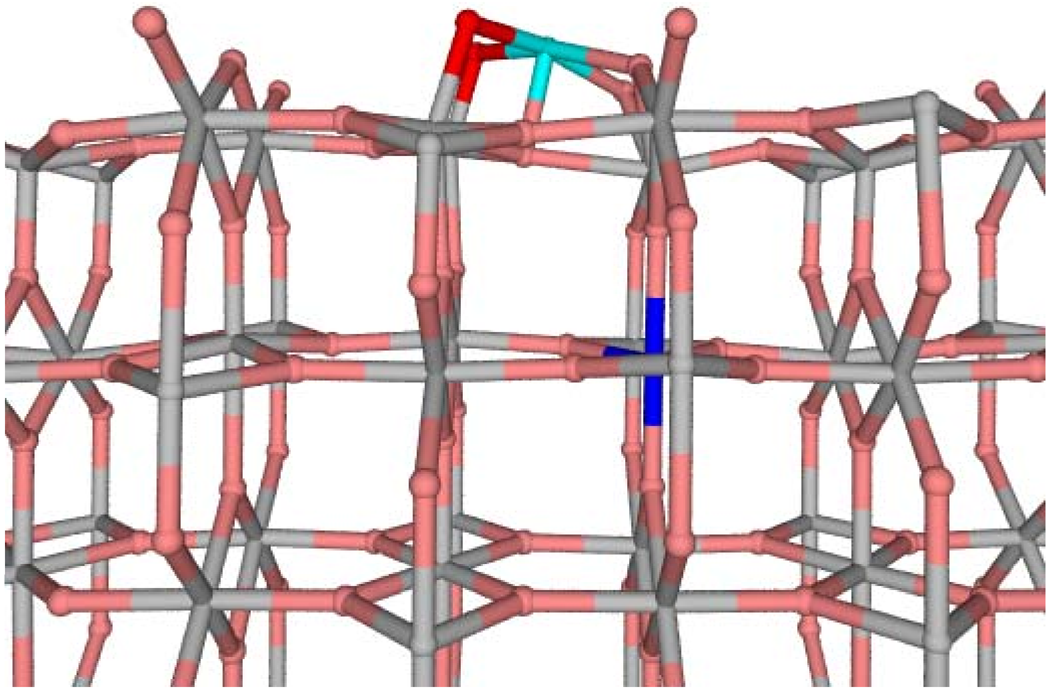
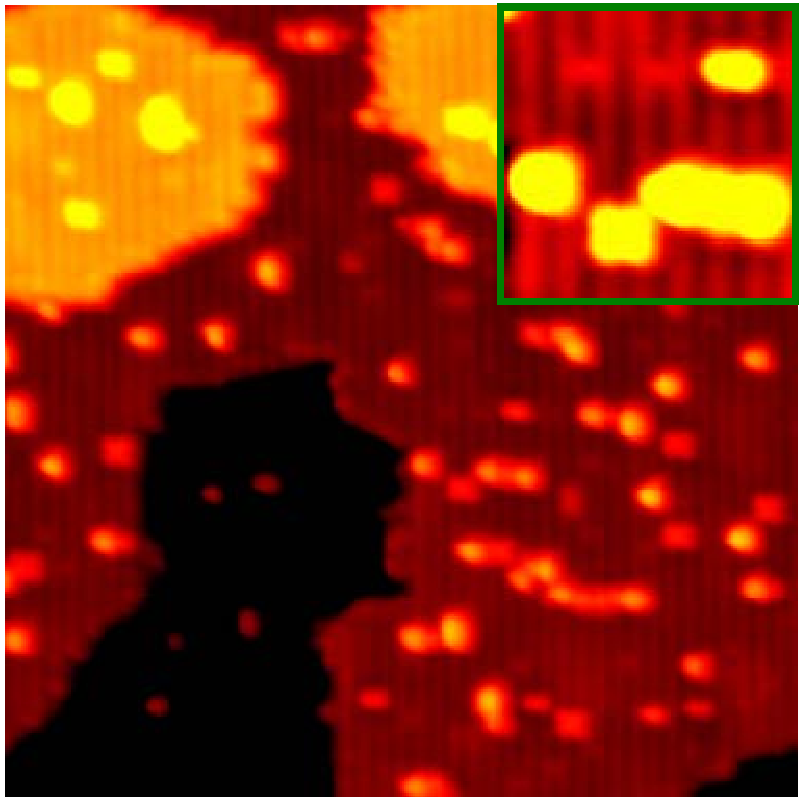
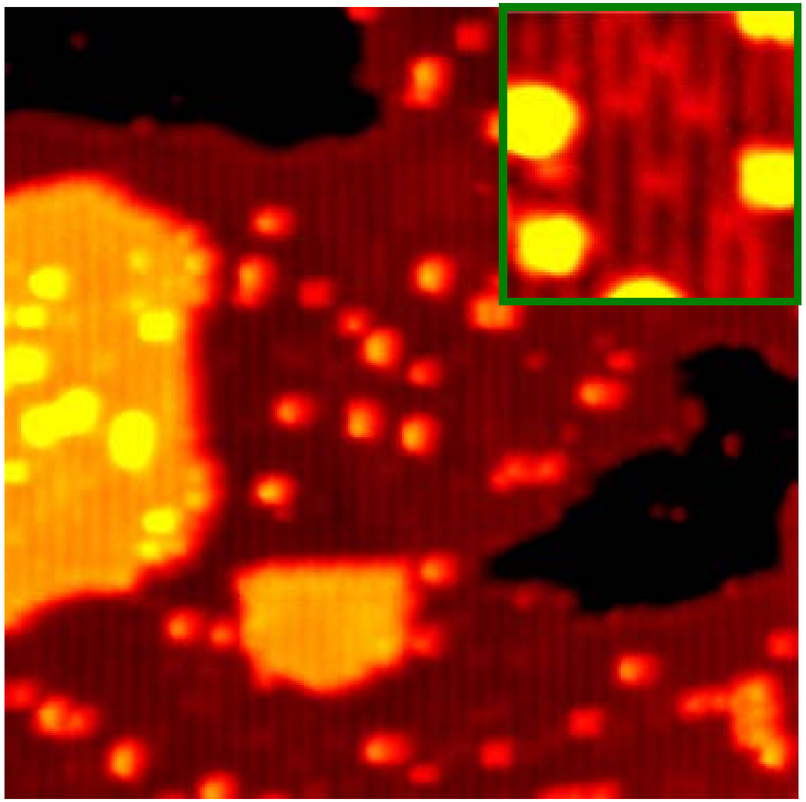
10
15
Reaction path (Å)



Ti diffusion toward the surface and: Formation of new TiO_x ad-structures



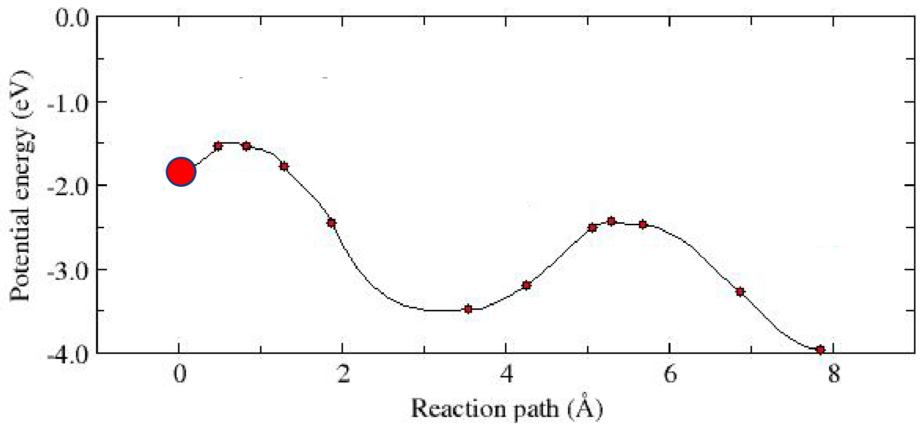
heated to 595 K



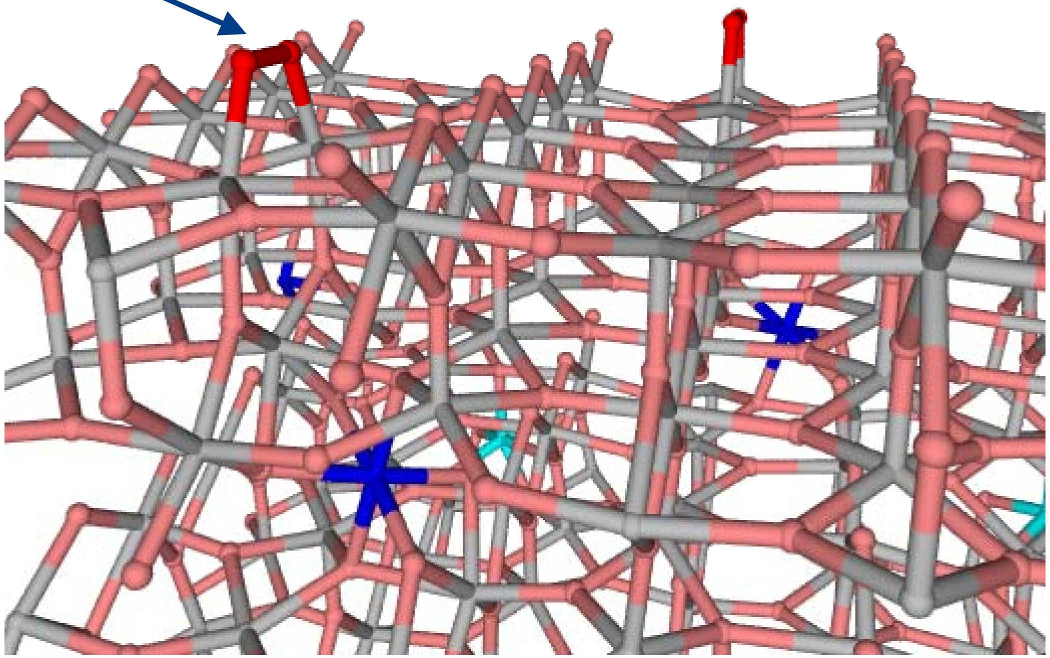
heated to 698 K

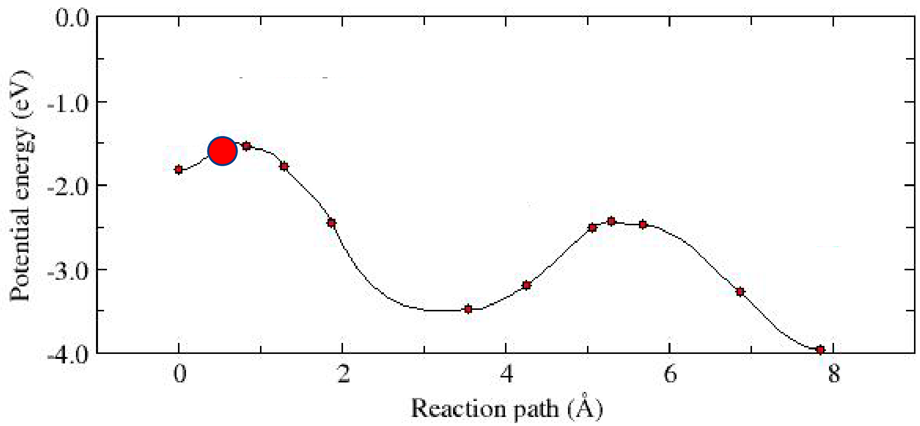
S. Wendt, …Bjørk Hammer, F. Besenbacher, Science 320, 1755 (2008)

DFT:



O_2 molecule

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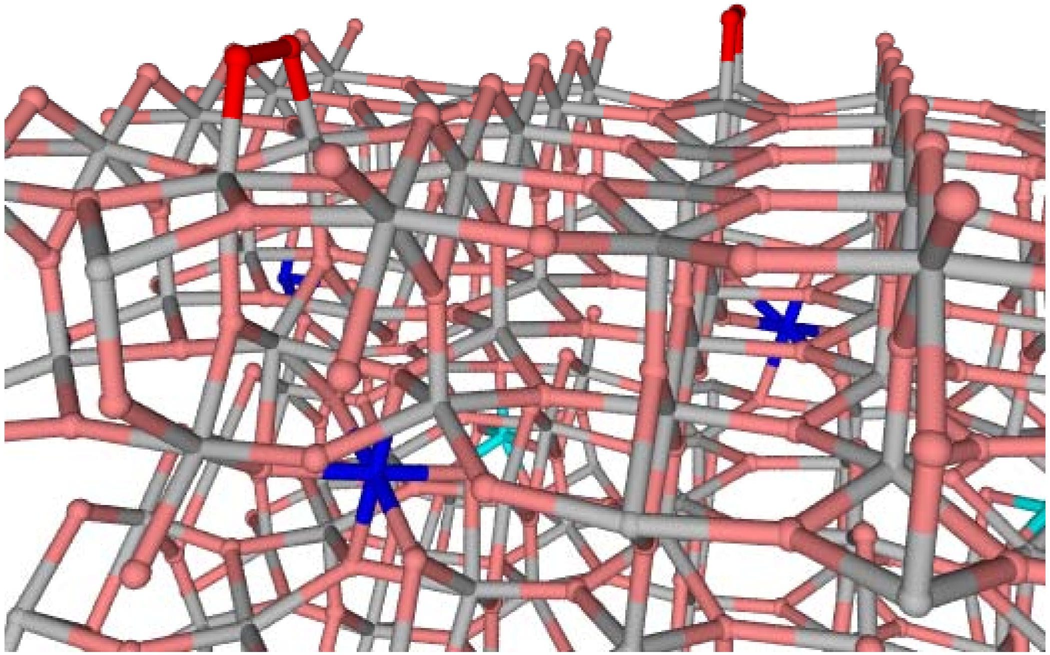
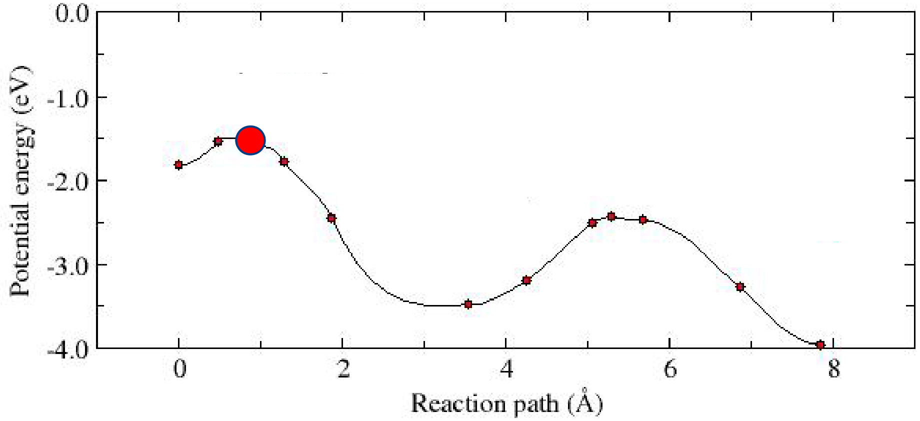
Potential energy (eV)
0
2
4
6
8
Reaction path (Å)

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Potential energy (eV)
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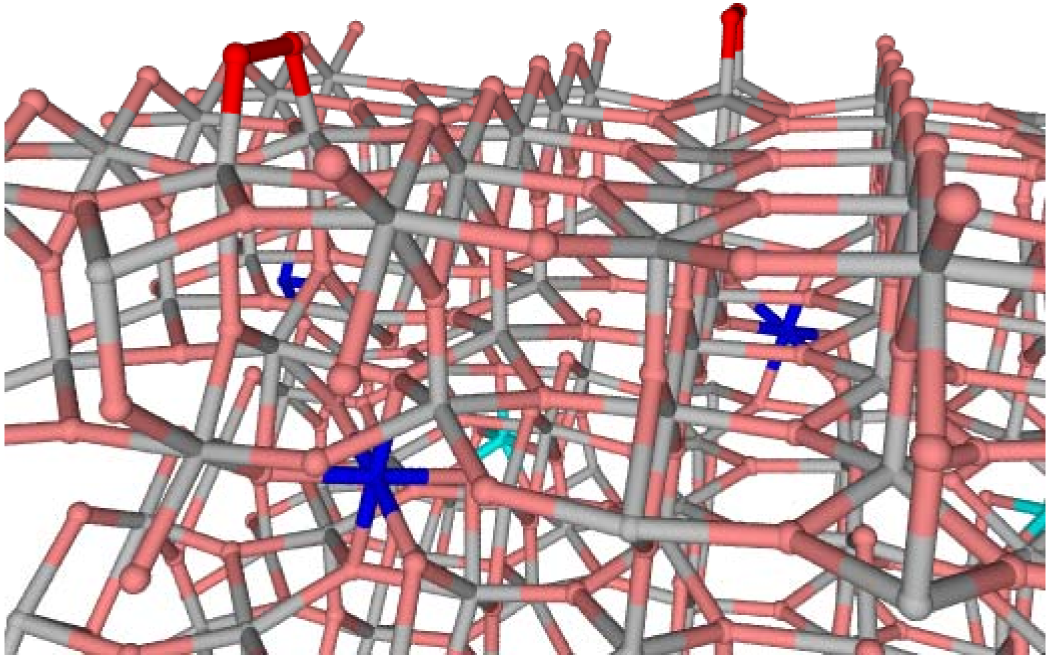
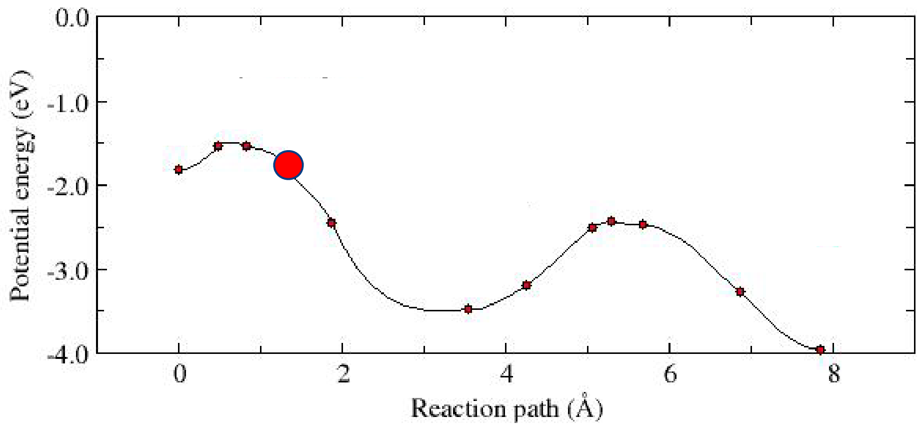
Reaction path (Å)





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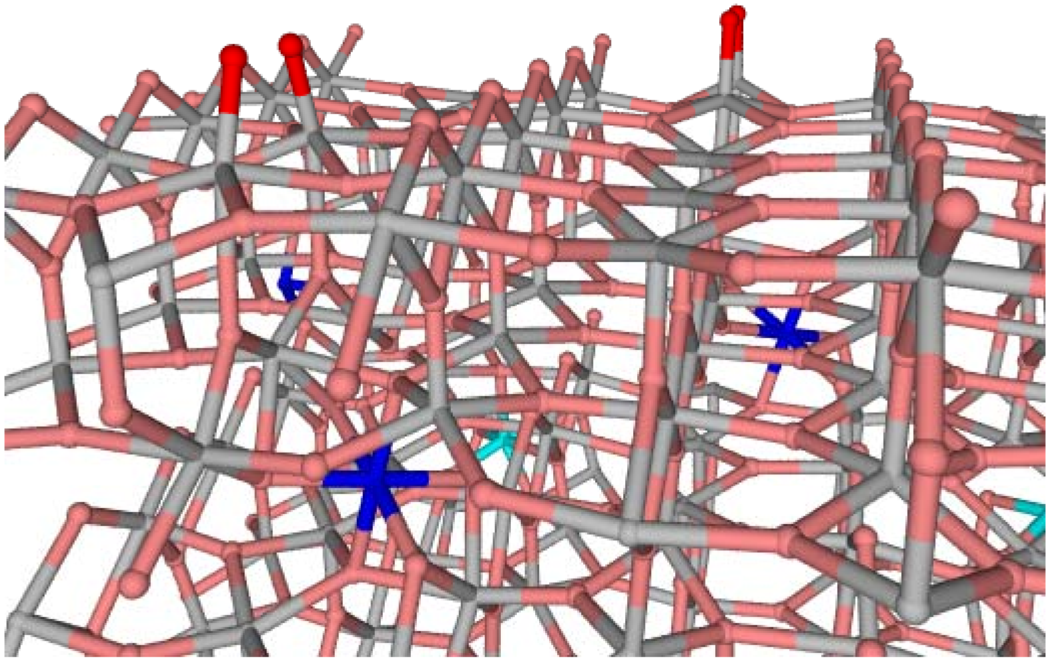
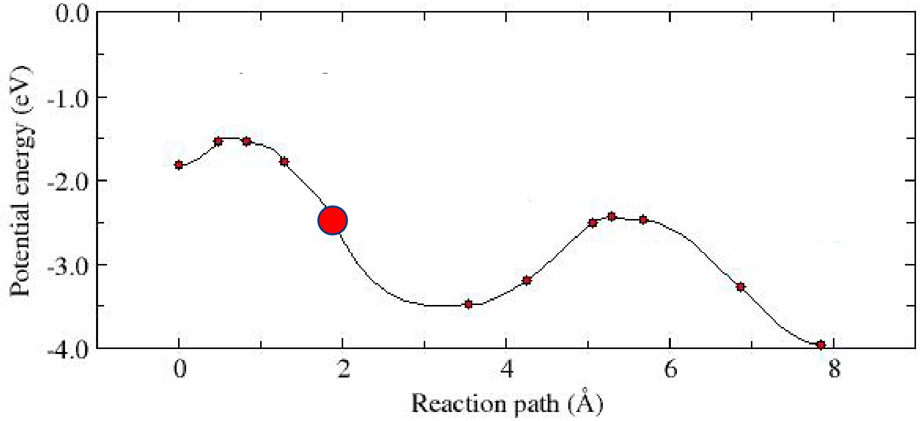
Potential energy (eV)
Reaction path (Å)

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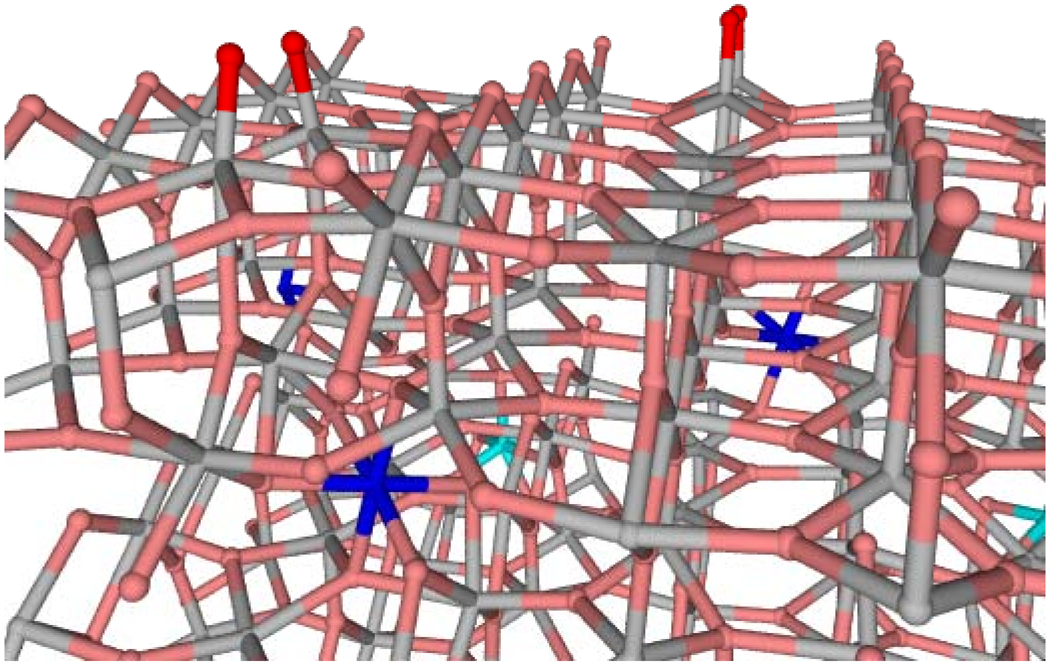
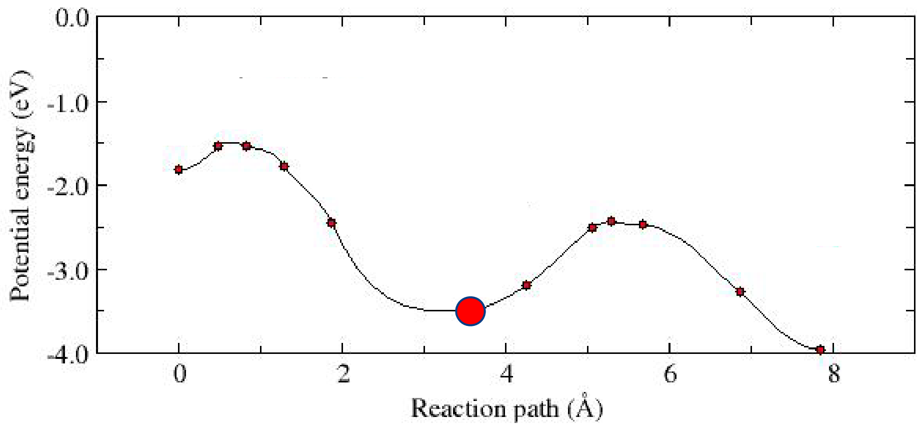
Reaction path (Å)

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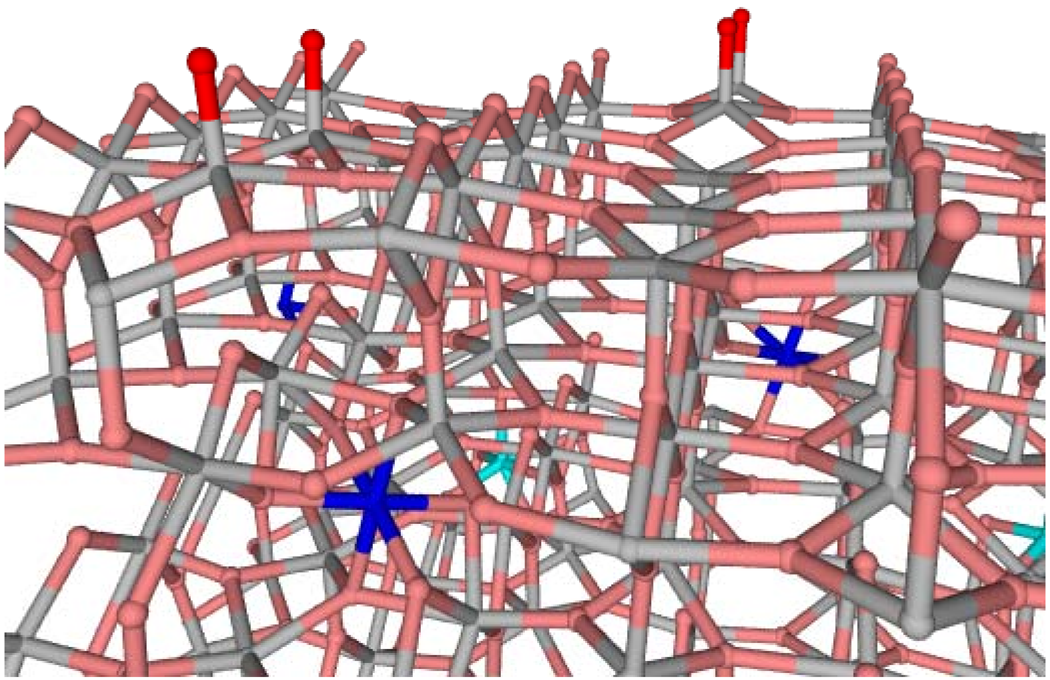
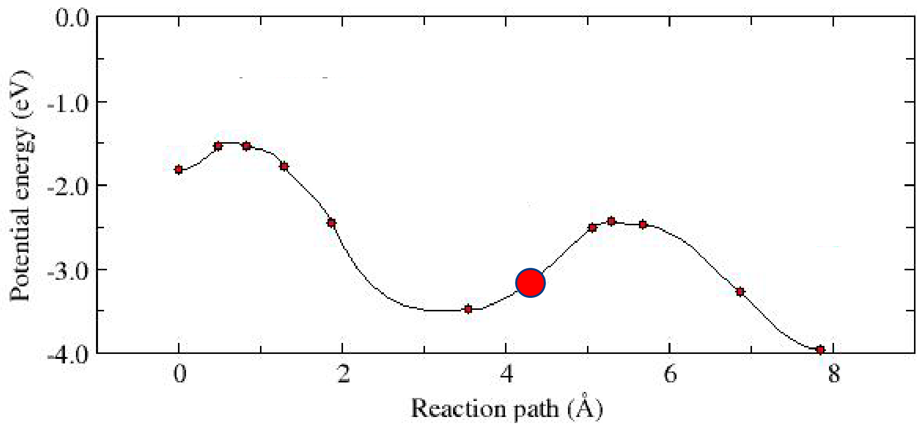
Potential energy (eV)
Reaction path (Å)

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Potential energy (eV)
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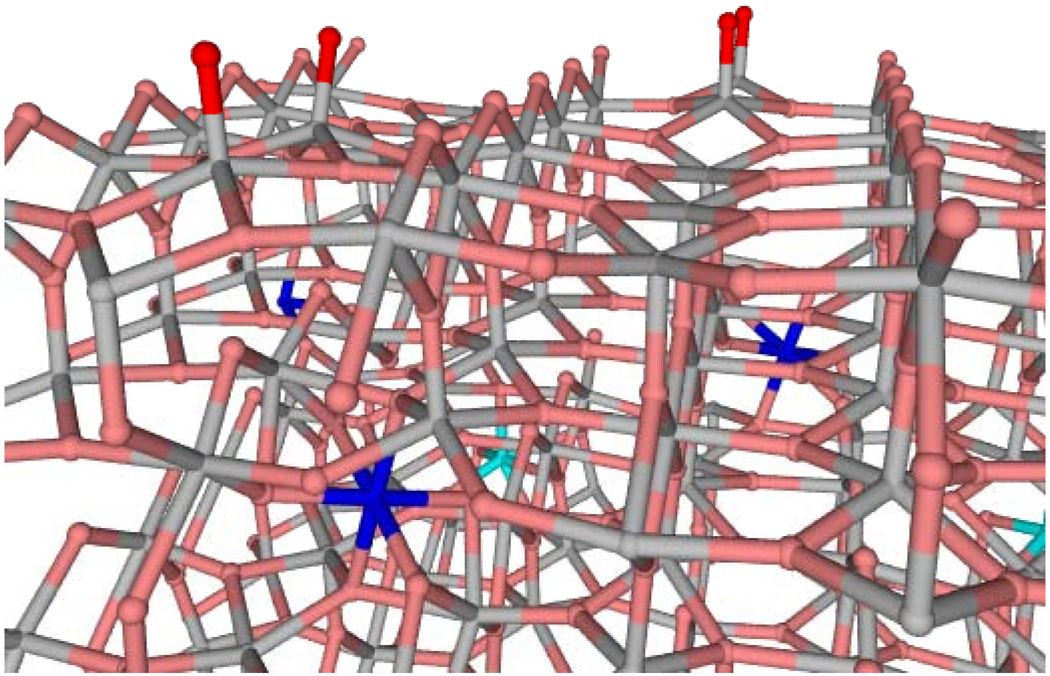
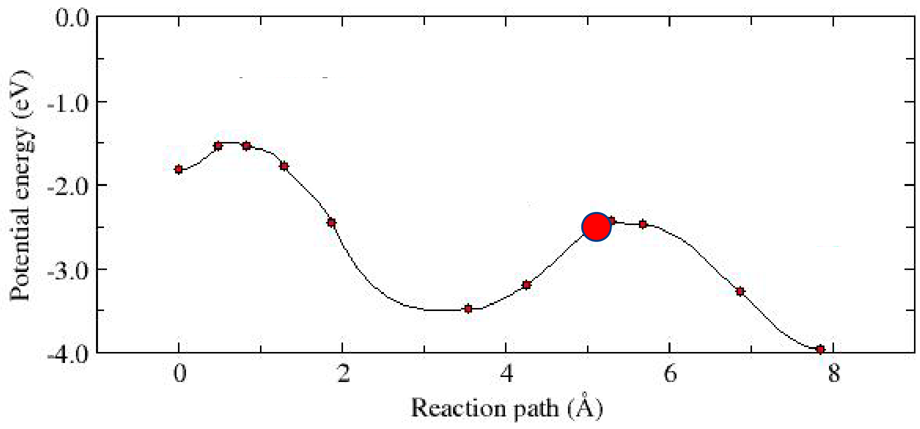
Reaction path (Å)

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Potential energy (eV)
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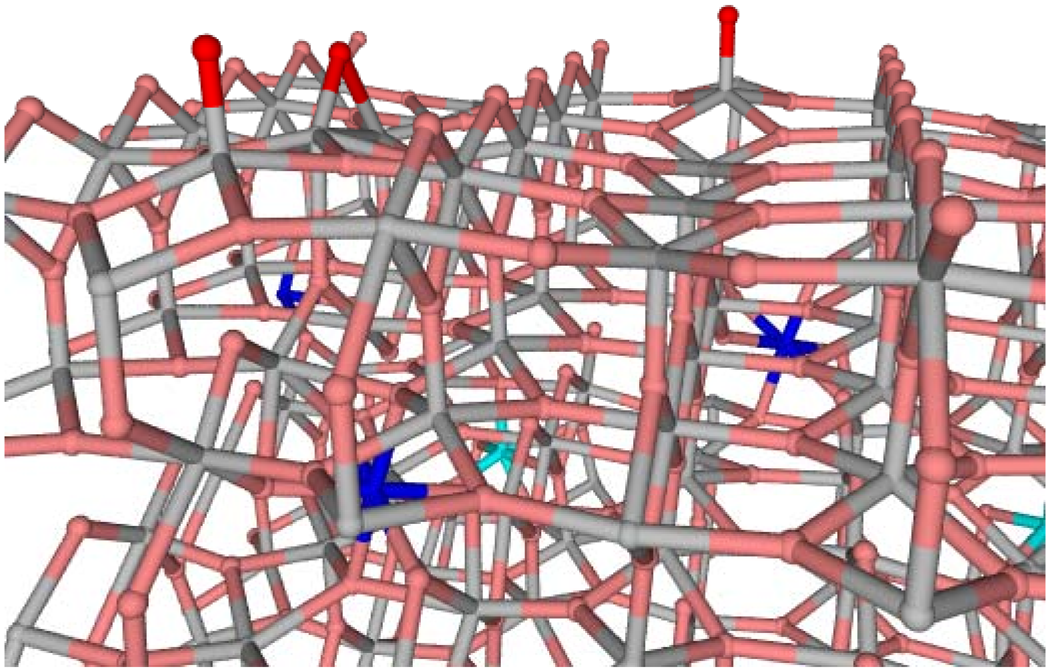
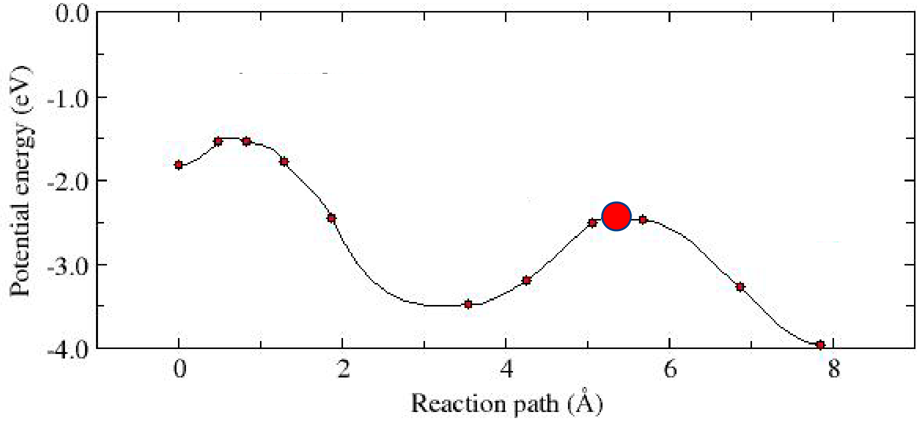
Reaction path (Å)

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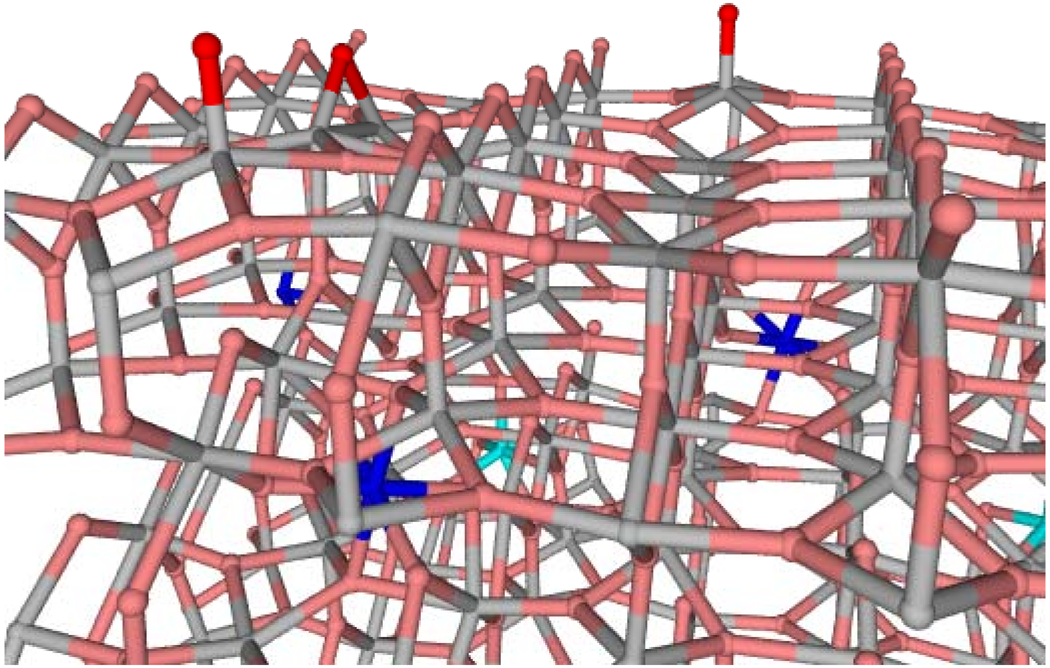
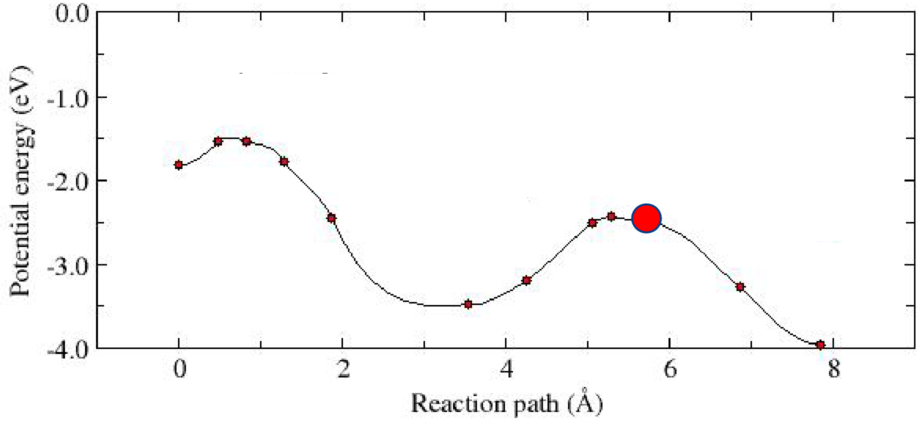
Reaction path (Å)

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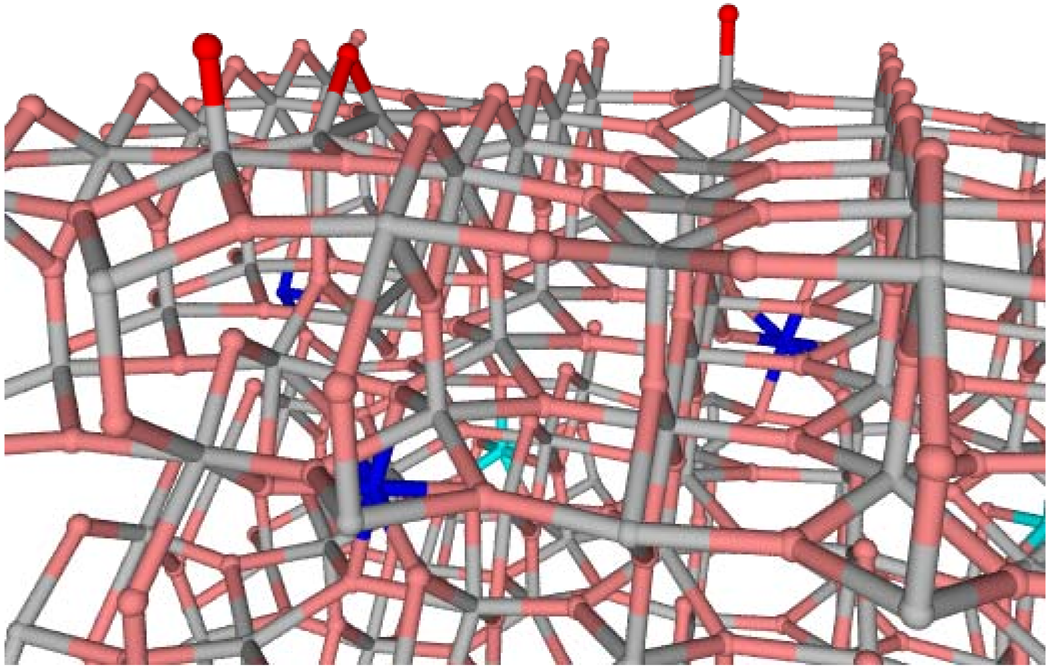

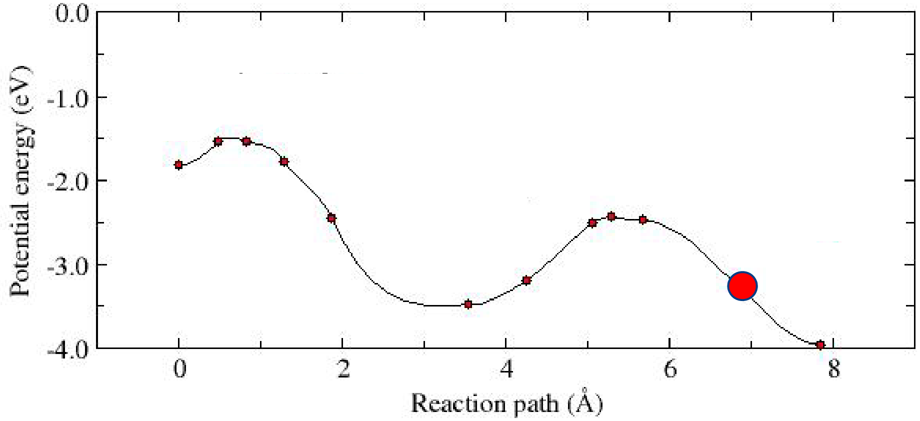
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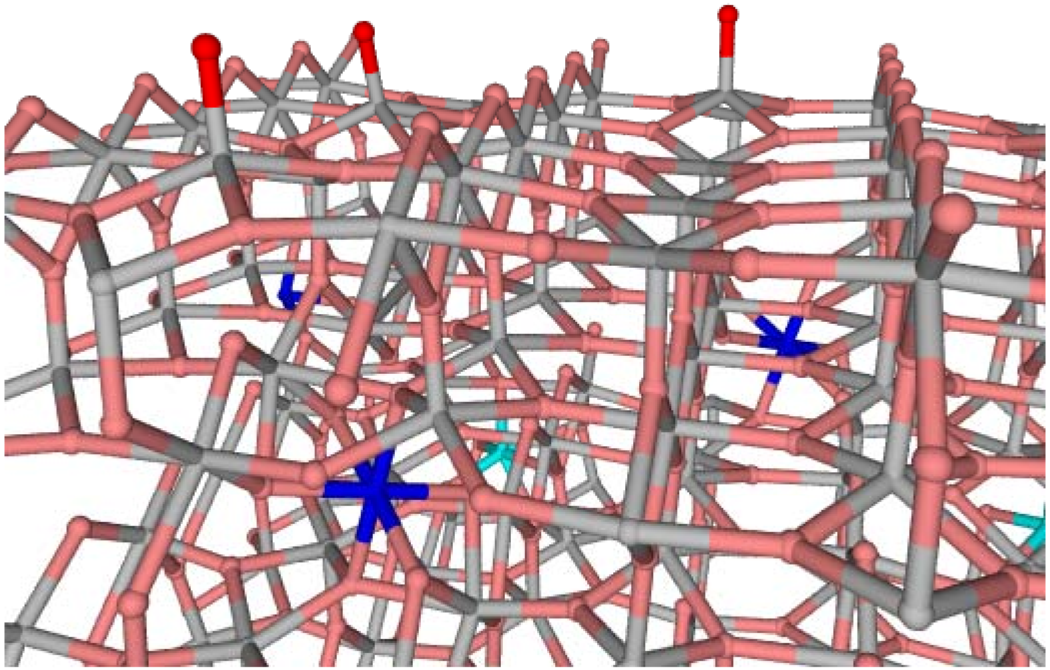
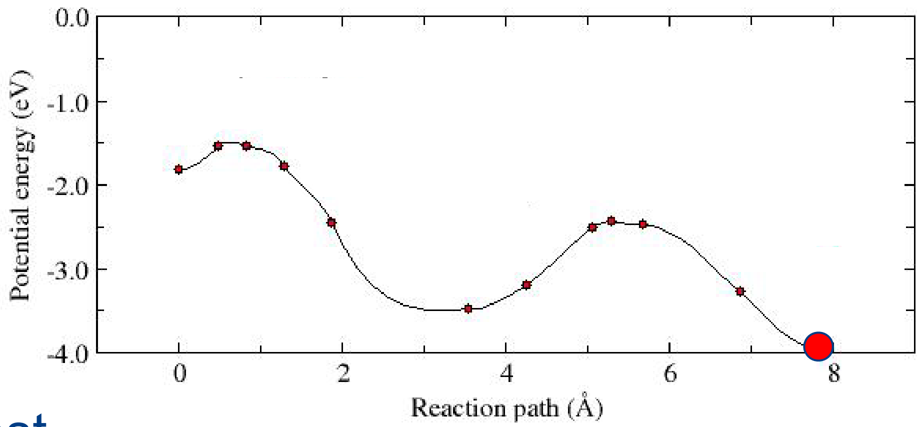
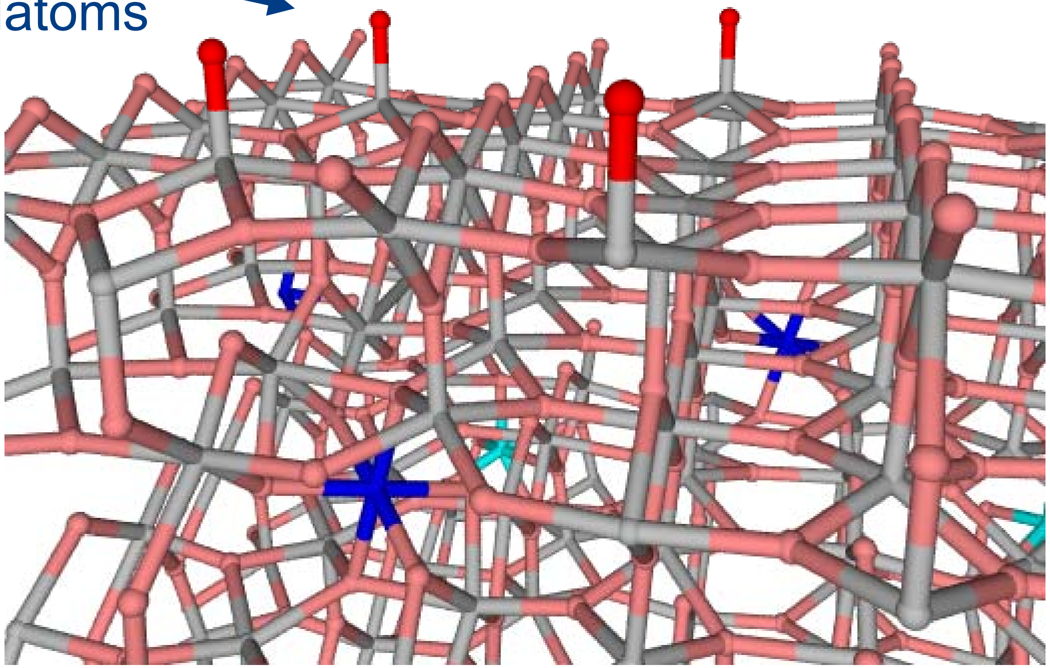
Reaction path (Å)



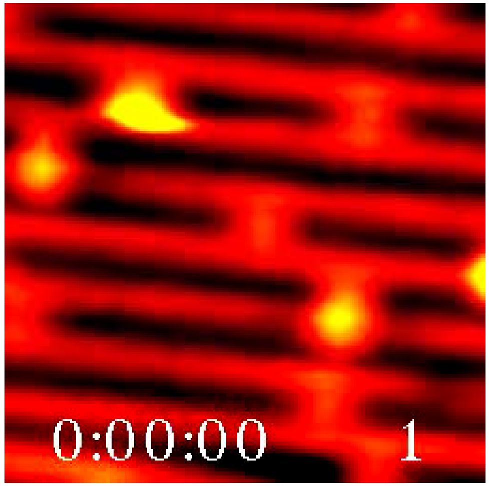


Pair of next-nearest neighbor O_{ot} adatoms

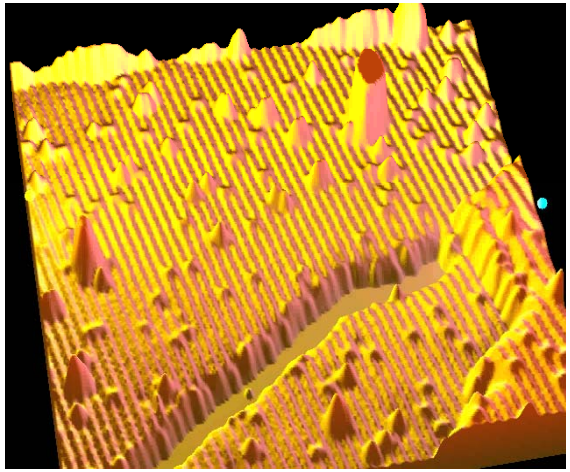


Take home message I

Defects (interstitials and vacancies) are of utmost importance for surface redox chemistry on reduced titania



Thanks to



- S. Wendt,, J. Ø. Hansen, E. Lira, Peipei Huo, J. Matthiesen, R. Schaub, E. Lægsgaard
- Bjørk Hammer, J. Wang
- J. V. Lauritsen, A. Tuxen, H. Goebel, J. Kibbsgaard
- Jens Nørskov, Sibylle Gemming
- B. Hinneman, B. Clausen, H. Topsøe, S. Helveg

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