Heterogeneous catalysis

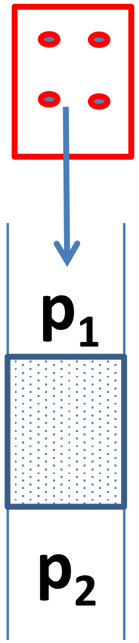
Lecture 4

Catalyst synthesis – continuation

- Shaping
- Single site catalysts

Shaping

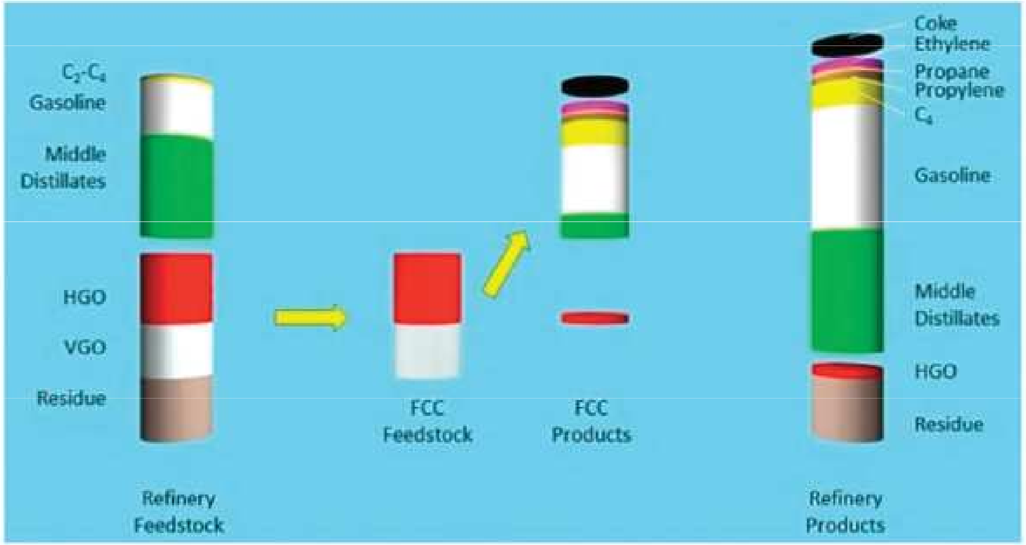
- Why is shaping important?
  - Accessibility (micro+meso+macro porosity)
  - Mechanical resistance (application of binders)
  - Reducing pressure drop ($p_1 > p_2$)
  - Hydrothermal stability, coking, poisoning,...

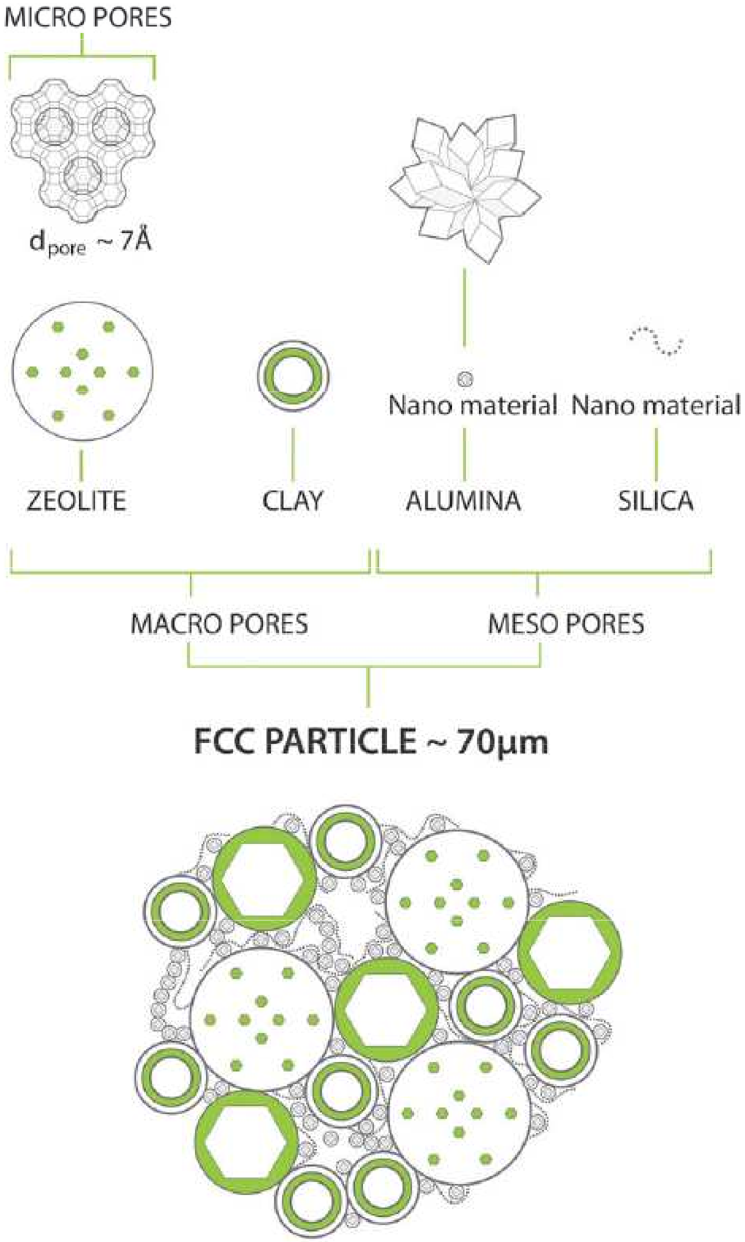


→ **Industrial point of view**

Shaping

- Industrial example: Fluid catalytic cracking

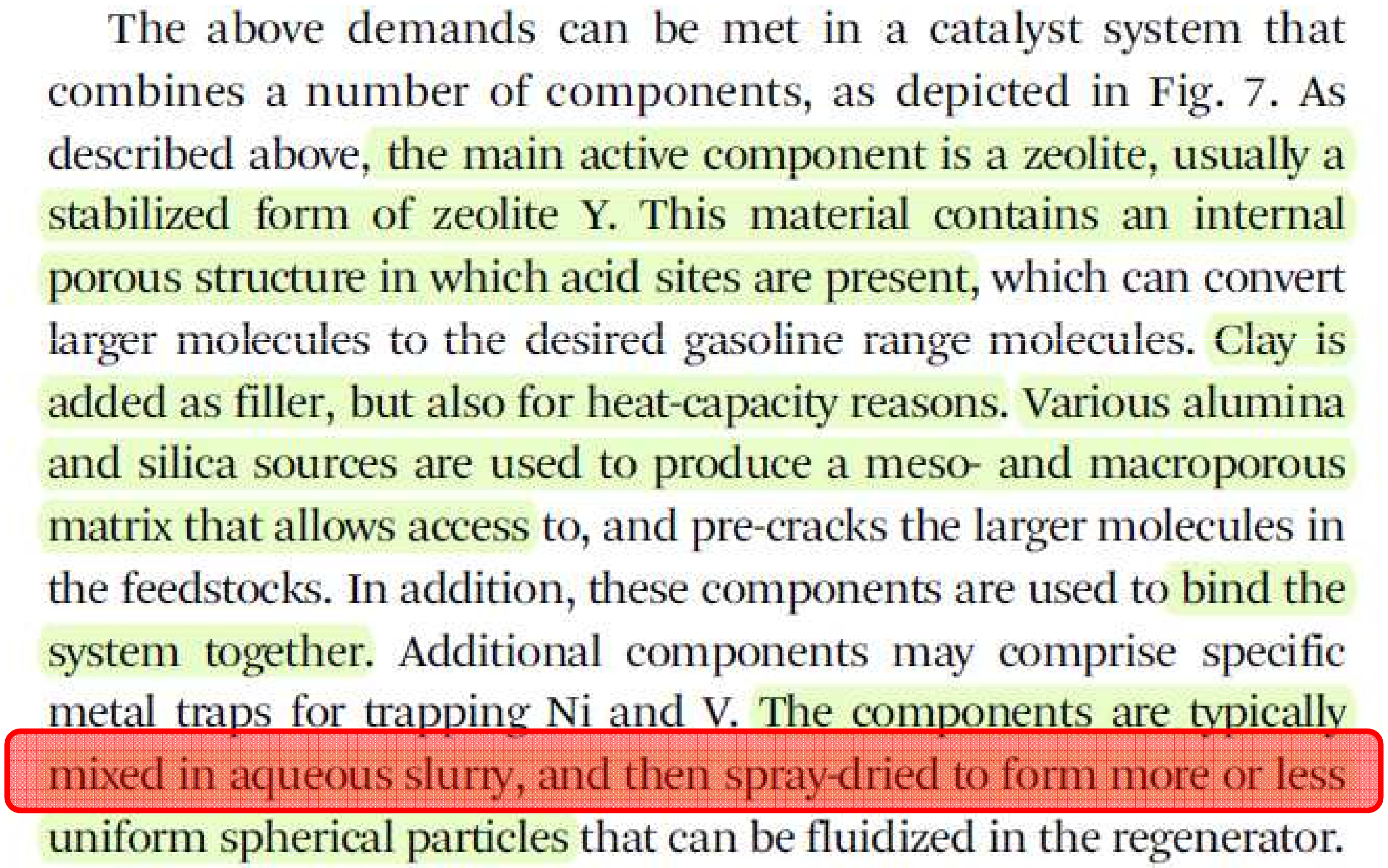




Chem. Soc. Rev., 2015, **44**, 7342–7370

Shaping

- Fluid catalytic cracking

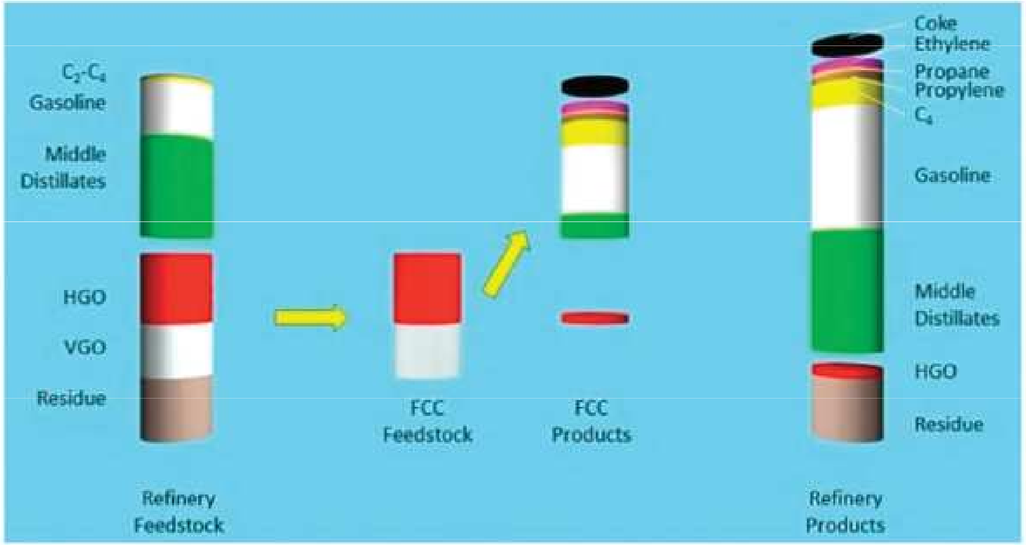


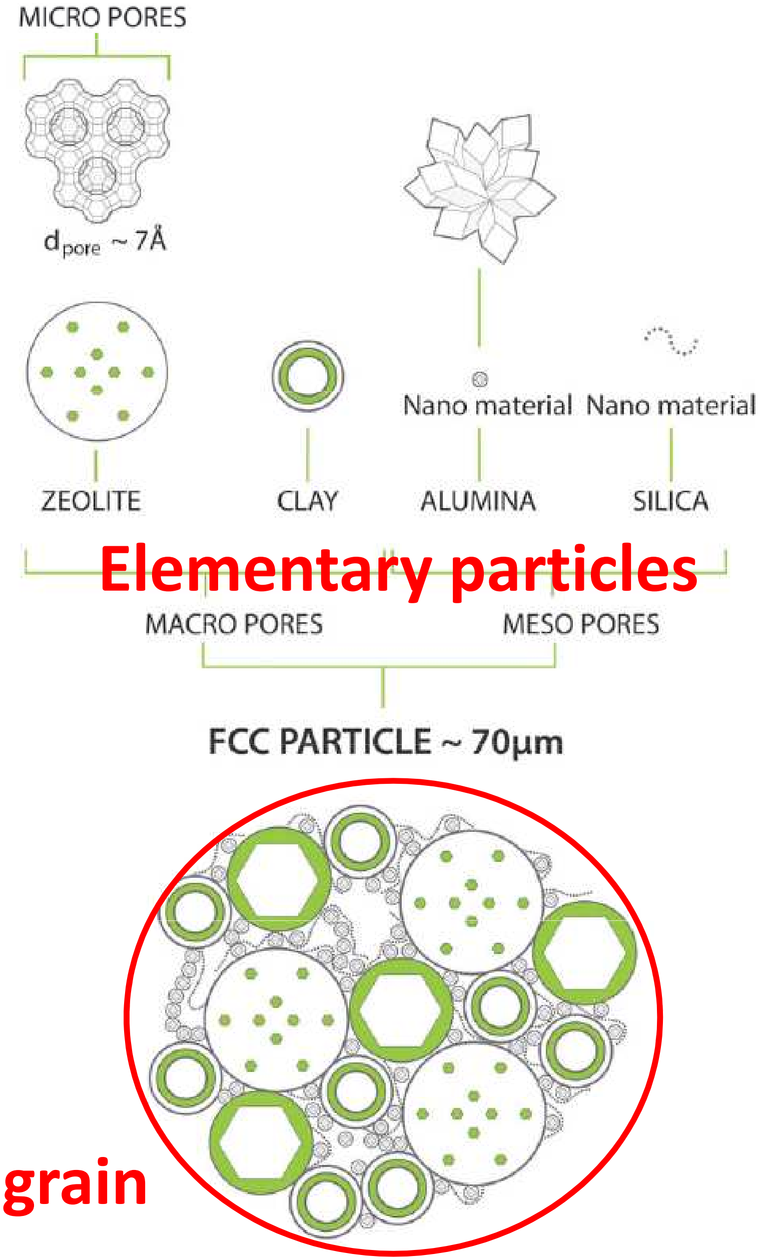
The above demands can be met in a catalyst system that combines a number of components, as depicted in Fig. 7. As described above, the main active component is a zeolite, usually a stabilized form of zeolite Y. This material contains an internal porous structure in which acid sites are present, which can convert larger molecules to the desired gasoline range molecules. Clay is added as filler, but also for heat-capacity reasons. Various alumina and silica sources are used to produce a meso- and macroporous matrix that allows access to, and pre-cracks the larger molecules in the feedstocks. In addition, these components are used to bind the system together. Additional components may comprise specific metal traps for trapping Ni and V. The components are typically mixed in aqueous slurry, and then spray-dried to form more or less uniform spherical particles that can be fluidized in the regenerator.

„malaxed-agglomerated catalyst“

Shaping

- Industrial example:
  Fluid catalytic cracking

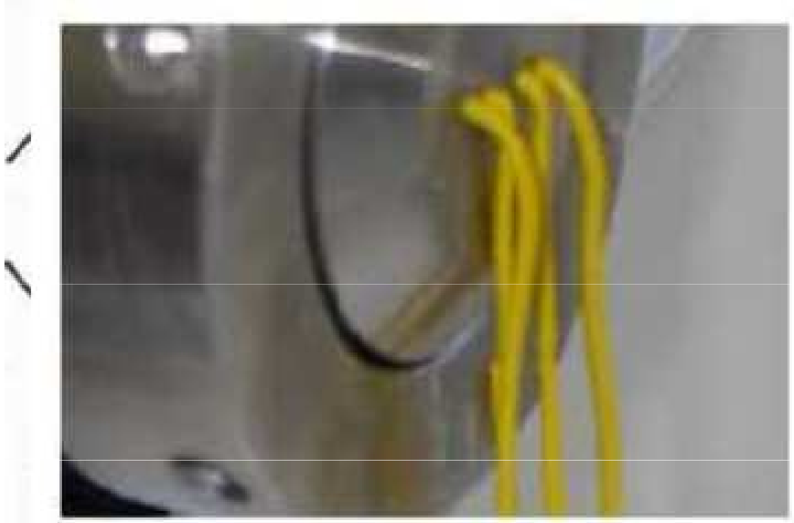


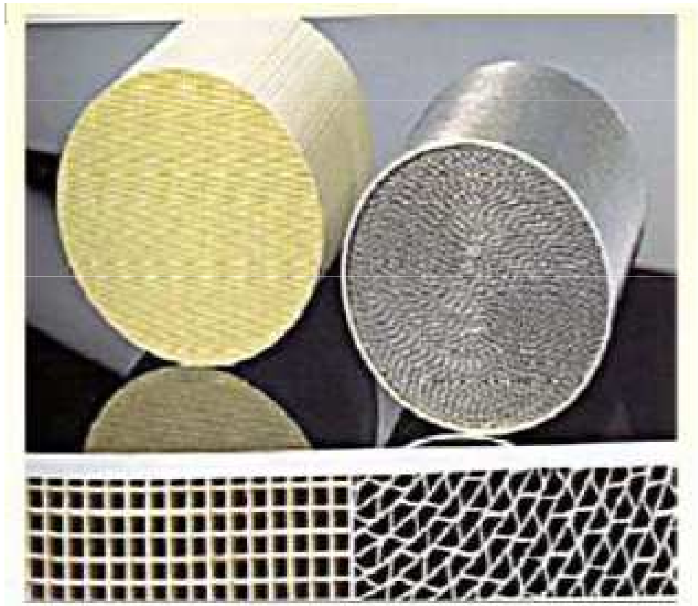


Chem. Soc. Rev., 2015, **44**, 7342–7370

Shaping

- Macroscopic shaping
  - – Extrusion
  - – Pelletization
  - – Molding/casting





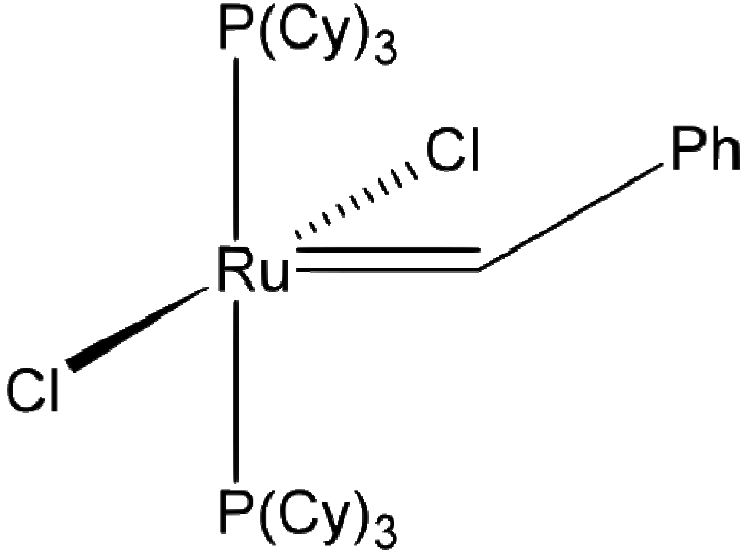
grain

Shaping

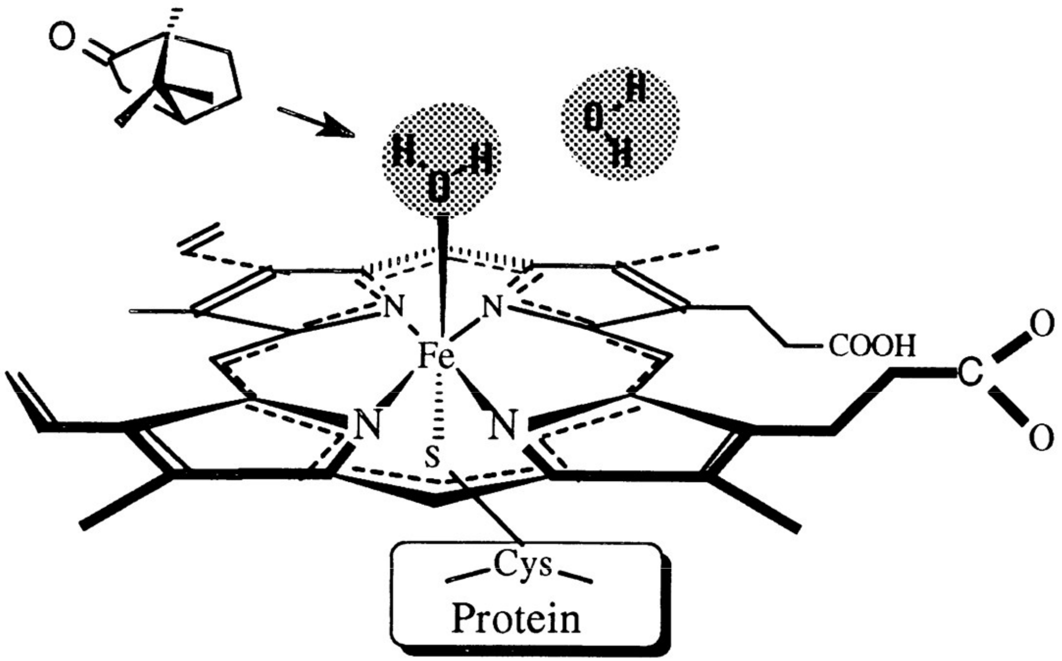
- Shaping as a „mechanochemical synthesis“?

Single site catalysts

- What is it?



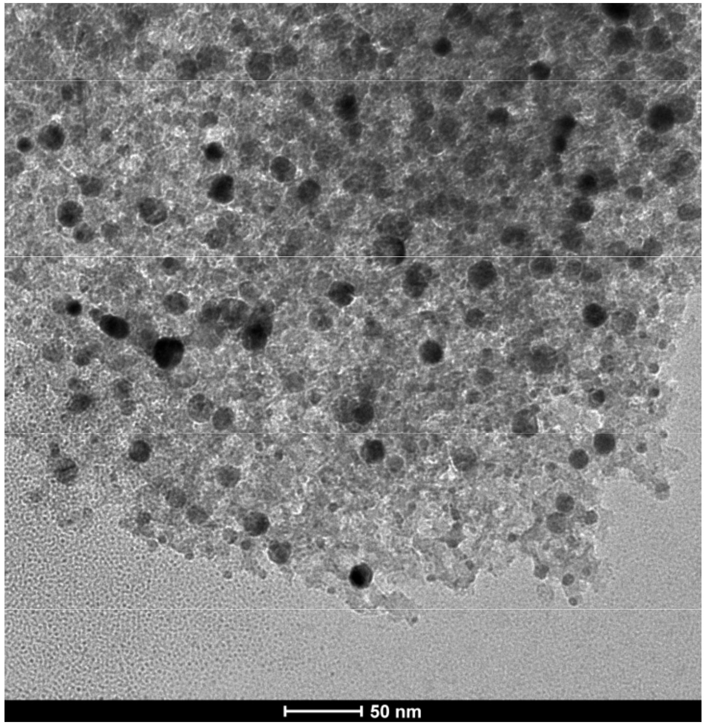
Grubbs catalyst
Homogeneous catalysis

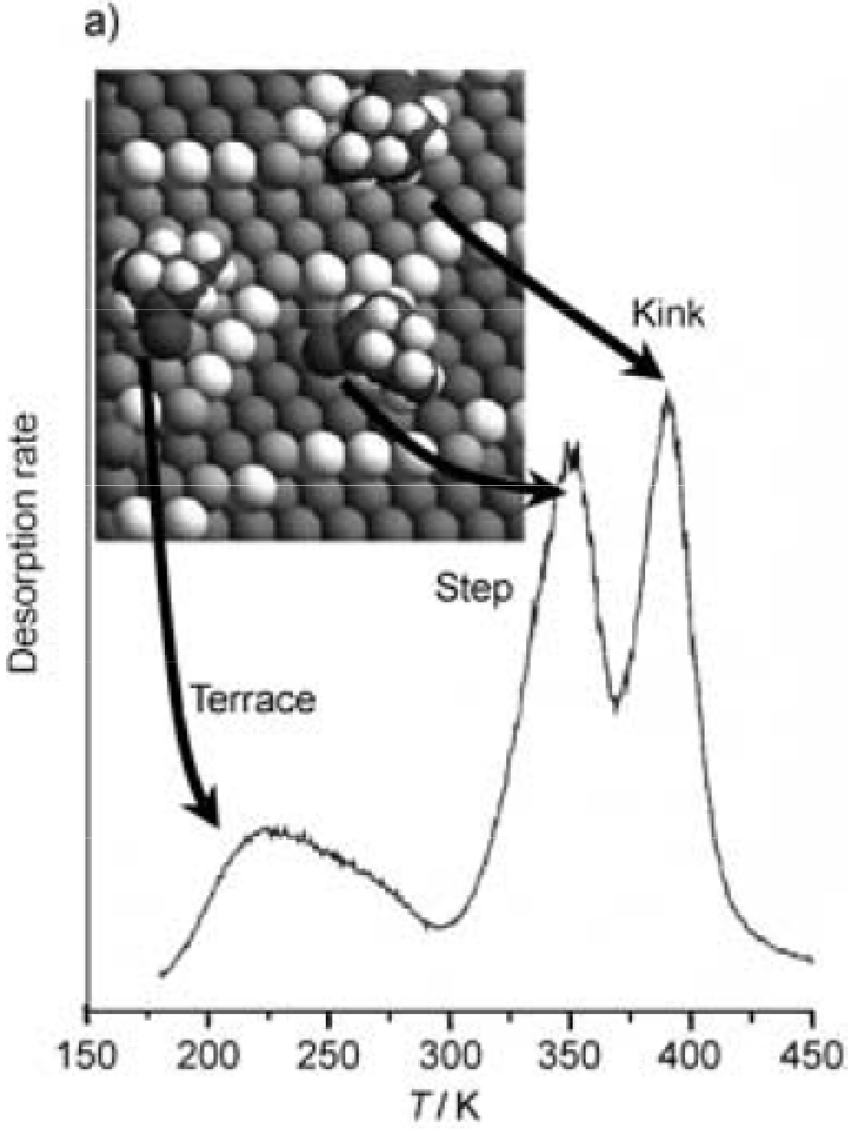


Active site in cytochrome P450
Enzymatic catalysis

Single site catalysts

- What is it?



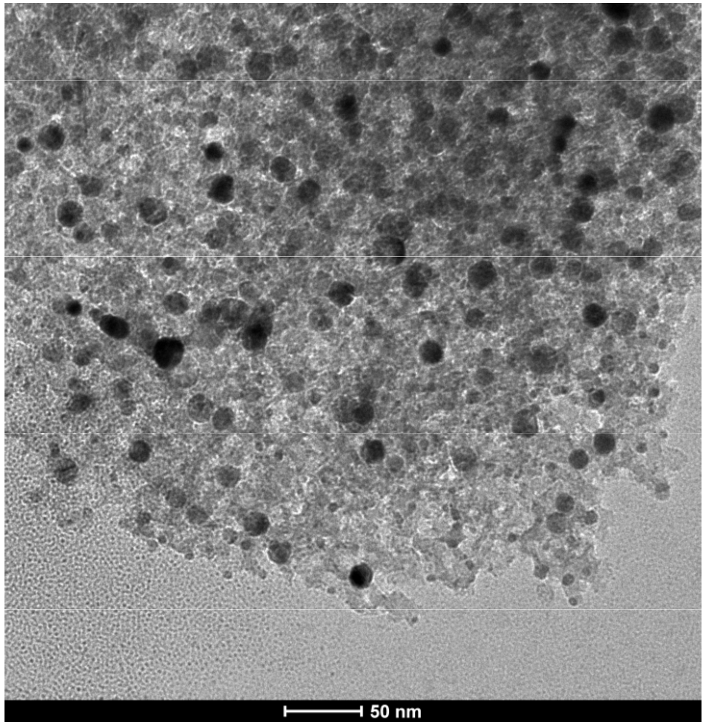


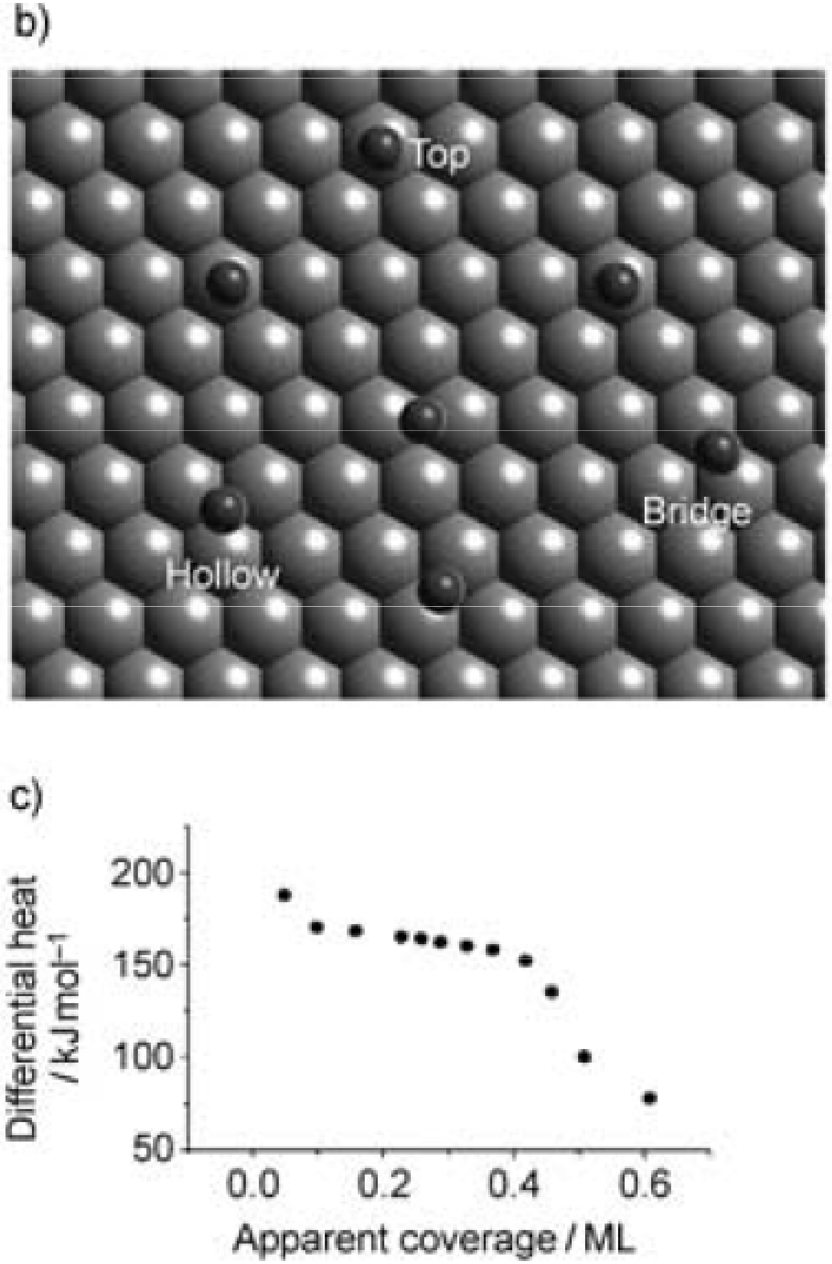
Phys. Chem. Chem. Phys., 2014, **16**, 7647–7661

Angew. Chem. Int. Ed. **2005**, *44*, 6456 – 6482

Single site catalysts

- What is it?





Phys. Chem. Chem. Phys., 2014, **16**, 7647–7661

Angew. Chem. Int. Ed. **2005**, 44, 6456 – 6482

Single site catalysts

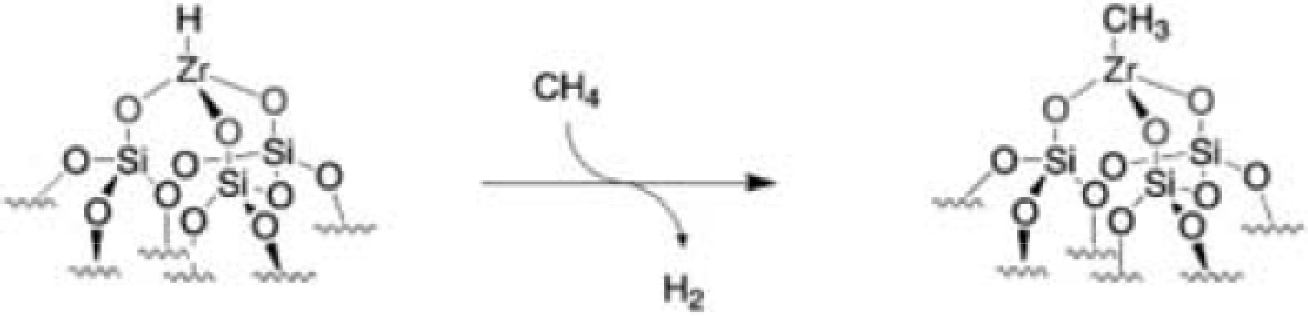
- Any continuous material (metal, oxide), where catalysis relies mainly on structure deffects
- Instead
  - One (or more) atoms
  - Spatially isolated
  - Same energy of interaction with reactant
  - Structurally well characterized (similar to homo)

Single site catalysts

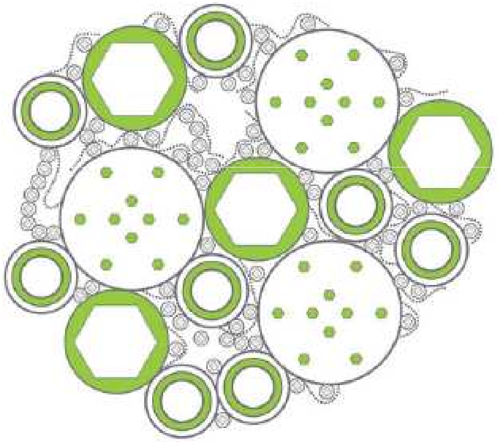
- What is it?
  - Individual isolated ion/atom/molecular complex/cluster
    - Grafted on porous support
    - Created within the material by building block approach
  - „Ship in bottle“ structures– e.g. molecular complex/enzyme trapped within a zeolitic cage
  - Crystalline, open-structure, microporous solids (e.g. zeolites) with active sites uniformly distributed throughout the bulk

Single site catalysts

- Why?



FCC PARTICLE ~ 70µm



Single site catalysts

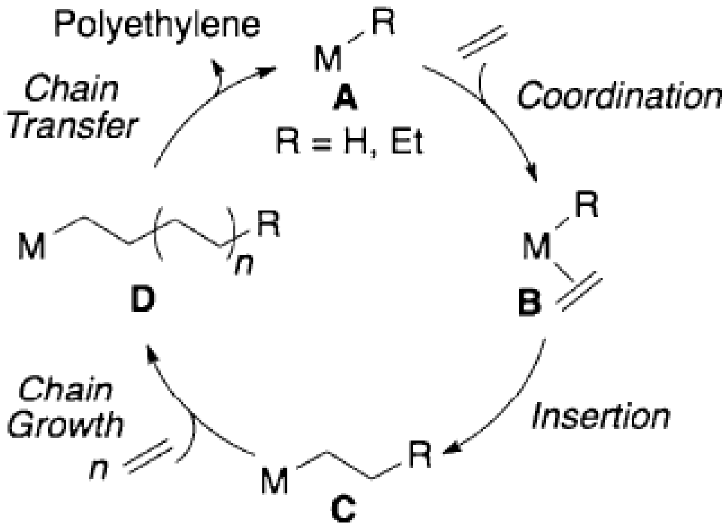
- Why?
  - Number of active sites
  - Turn-over frequency, TOF
  - Characterization of active site
  - Quantum-chemical calculations

  ↓
  - Understanding mechanism
  - Understanding kinetics

  ↓
  - Bridging gap between homo-and heterogeneous cata

Single site catalysts

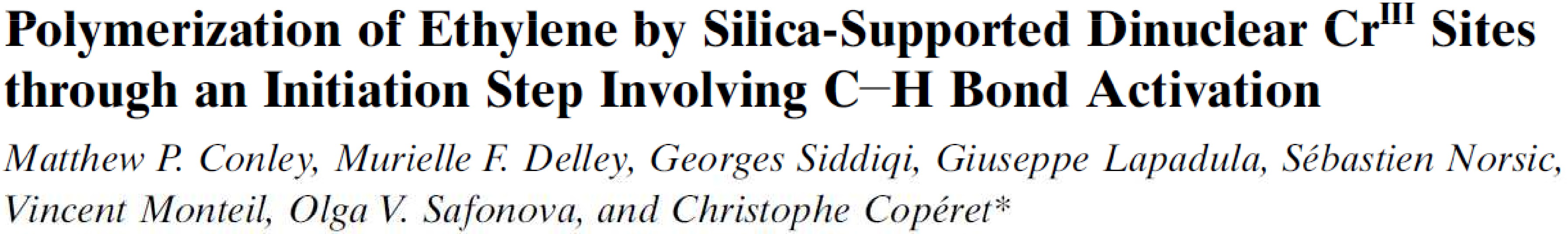
- Bridging gap between homogeneous and heterogeneous catalysis – **example**:
  - Phillips catalyst = „CrO_3“ dispersed on silica
  - Ethylene polymerization (50 % of global production of linear HDPE)
  - No co-catalyst (compare with Ziegler-Natta + MAO)
  - What is the actual active site???



Single site catalysts

- CrO_3 dispersed on silica
- Ethylene exposure induces „mild reduction“
- Only 10 % of Cr sites are active

- **Cr^{II} or Cr^{III}**??? Big discussion…



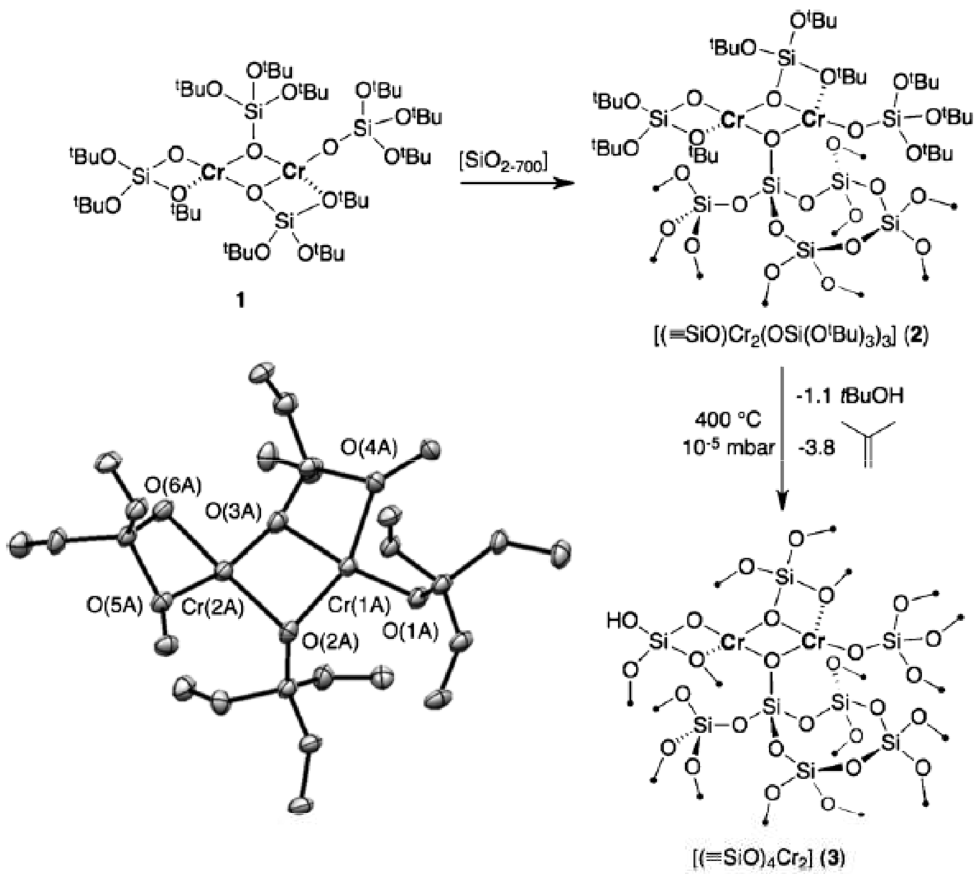
Polymerization of Ethylene by Silica-Supported Dinuclear Cr^{III} Sites through an Initiation Step Involving C–H Bond Activation

*Matthew P. Conley, Murielle F. Delley, Georges Siddiqi, Giuseppe Lapadula, Sébastien Norsic, Vincent Monteil, Olga V. Safonova, and Christophe Copéret**

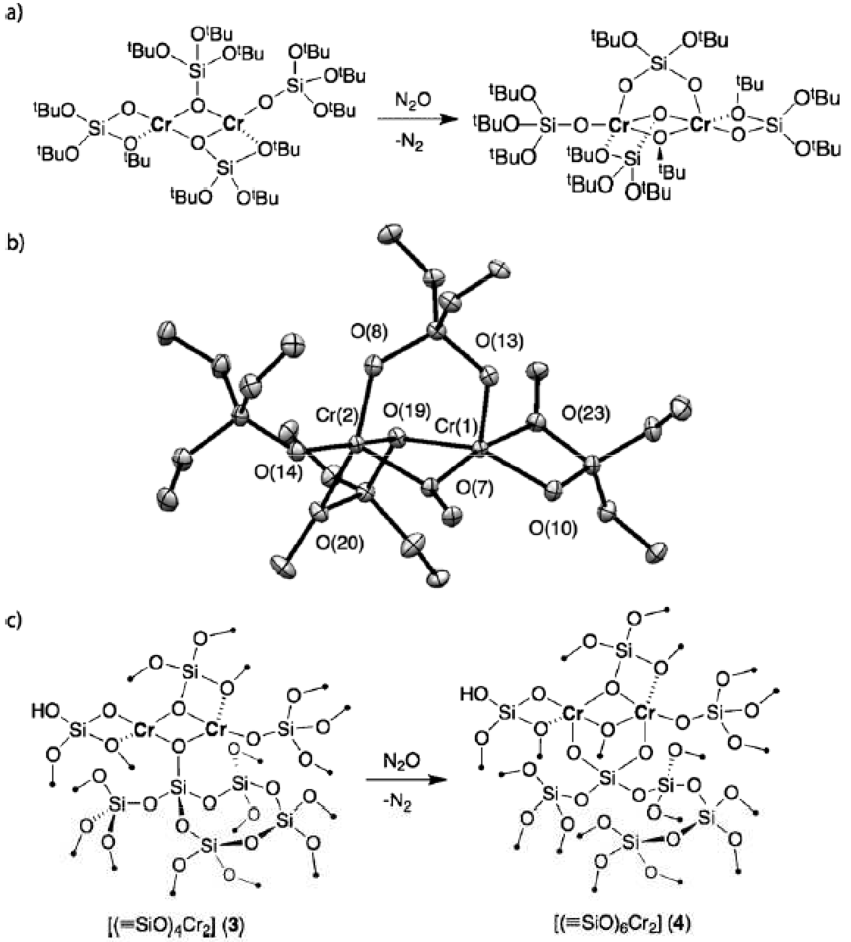
Single site catalysts

Cr^{II}

Cr^{III}



Scheme 2. Grafting of **1** on SiO_{2-700} to form $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**) and thermal decomposition under high vacuum to yield $[(\equiv SiO)_4Cr_2]$ (**3**). The solid-state structure obtained by X-ray diffraction for an independent molecule of **1** is shown at 50% probability. Methyl groups of $-OSi(OtBu)_3$ ligands and H atoms have been removed for clarity.



Scheme 3. a) Reaction of **1** with N_2O to give **5**. b) Solid-state structure of **5** as obtained by X-ray diffraction. Methyl groups of $-OSi(OtBu)_3$ ligands and H atoms have been removed for clarity. c) Surface rearrangement of $[(\equiv SiO)_4Cr_2]$ (**3**) to form $[(\equiv SiO)_6Cr_2]$ (**4**).

Single site catalysts

Cr^{III} is active!

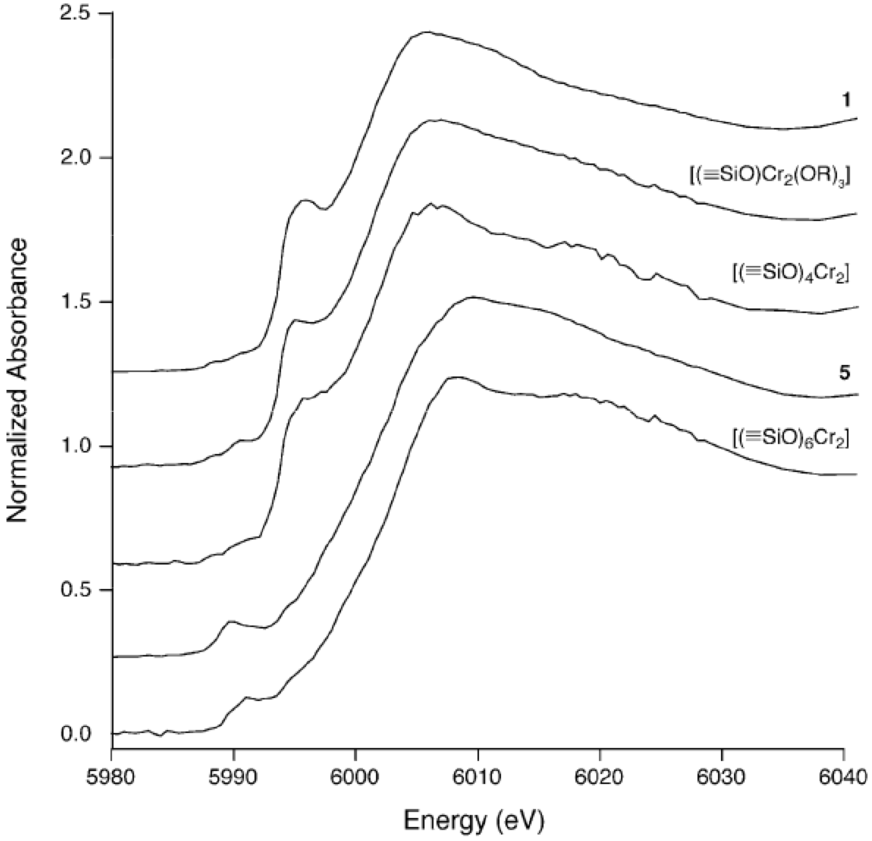
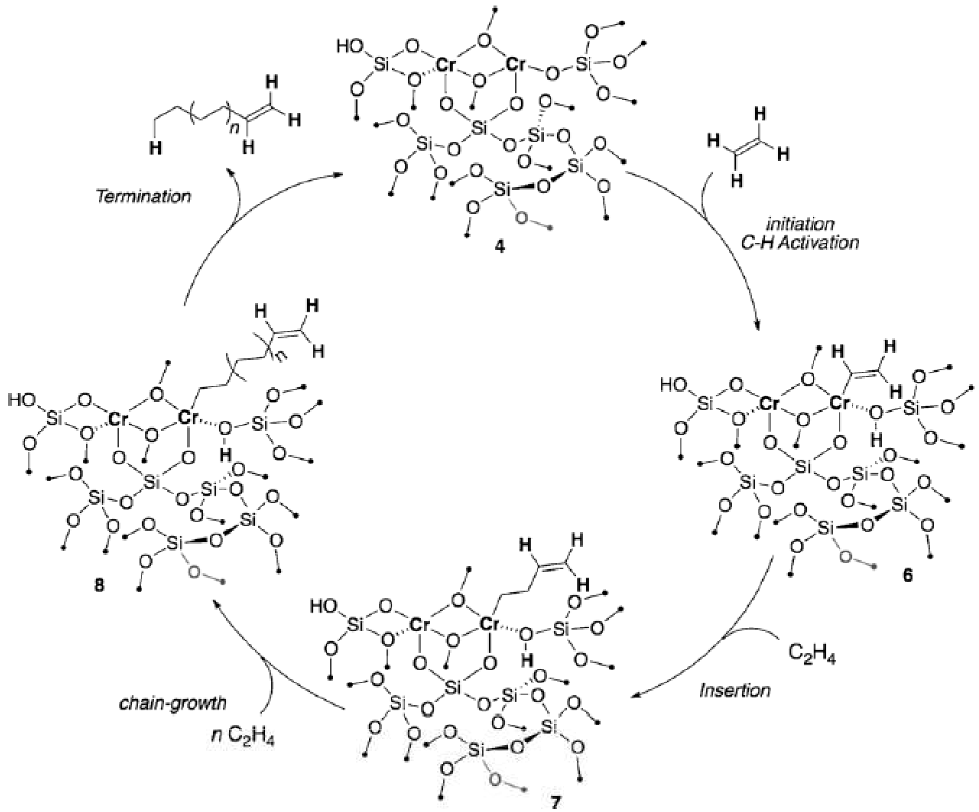


Figure 1. XANES spectra (collected in the transmission mode) of **1**, $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**), $[(\equiv SiO)_4Cr_2]$ (**3**), $[(\equiv SiO)_6Cr_2]$ (**4**), and **5**.



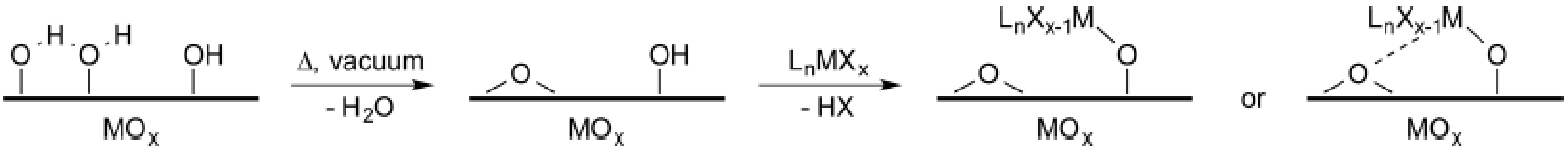
Scheme 4. Proposed mechanism for ethylene polymerization by $[(\equiv SiO)_6Cr_2]$.

Single site catalysts

- What is it?
  - **Individual isolated ion/atom/molecular complex/cluster**
    - **Grafted on porous support**
    - Created within the material by building block approach
  - „Ship in bottle“ structures– e.g. molecular complex/enzyme trapped within a zeolitic cage
  - Crystalline, open-structure, microporous solids (e.g. zeolites) with active sites uniformly distributed throughout the bulk

Single site catalyts

- Grafting on silica



  - Detailed knowledge of surface (number of OH groups per nm^2)
  - Rigorous water- and oxygen-free environment

DOI: 10.1021/acs.chemrev.5b00373
Chem. Rev. 2016, 116, 323–421

Single site catalysts

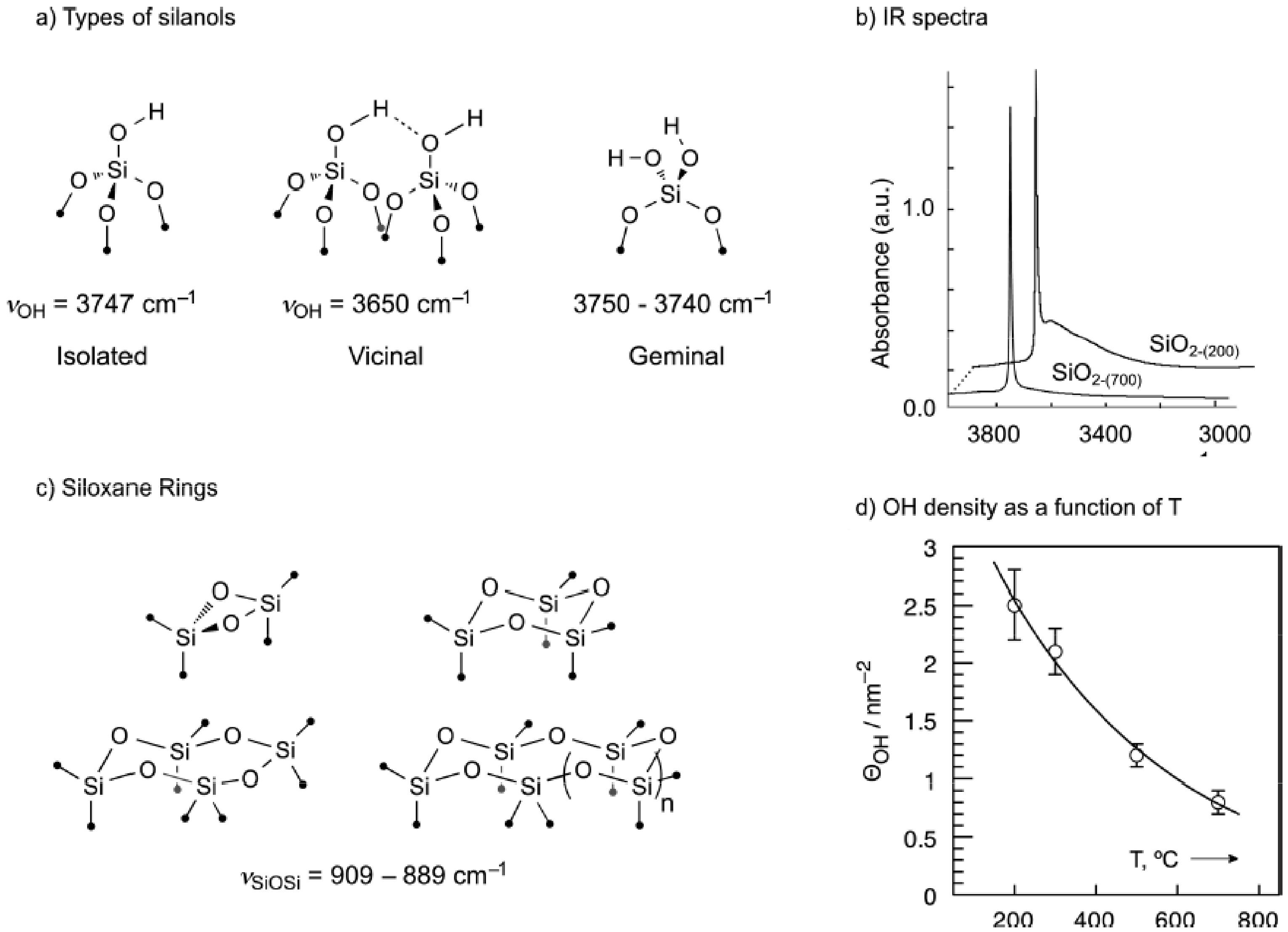


Figure 4. (a) Types of silanols. (b) Infrared spectra of Aerosil-200 partially dehydroxylated at 200 and 700 °C (SiO_{2-200} and SiO_{2-700}). (c) Siloxane rings. (d) Effect of temperature on surface OH density.

Single site catalysts

- Metal precursors (almost all d + f elements)
    - Organometallic compounds
    - Metal amides and silylamides
    - Metal alkoxides and siloxides
    - Metal halogenides

CHEMICAL REVIEWS

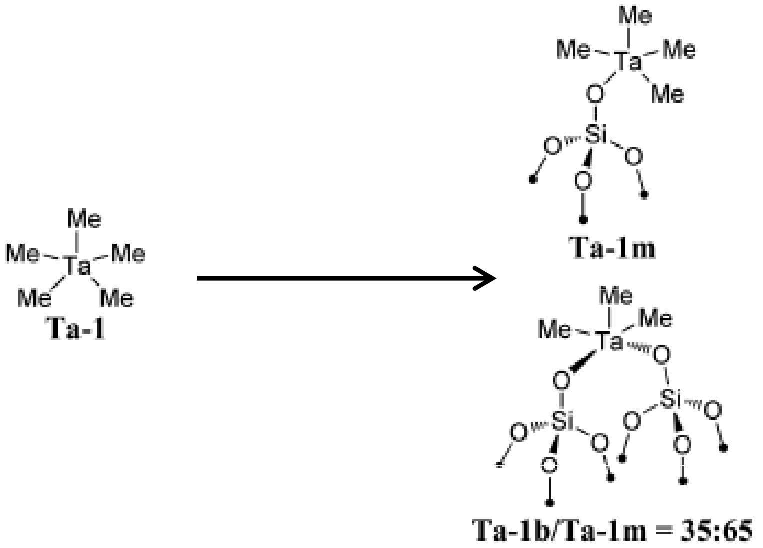
Review

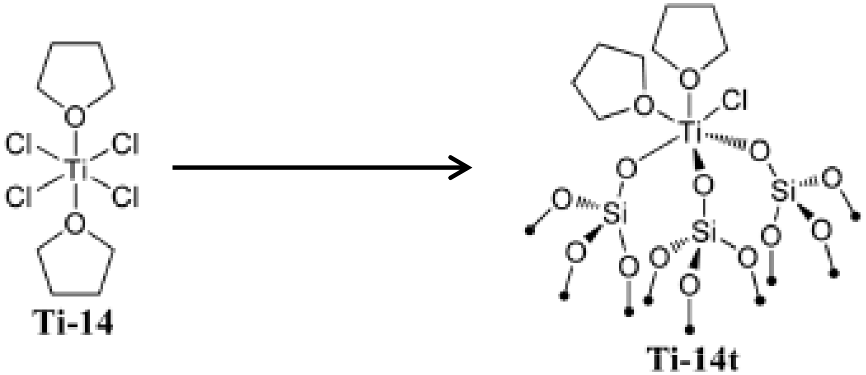
pubs.acs.org/CR

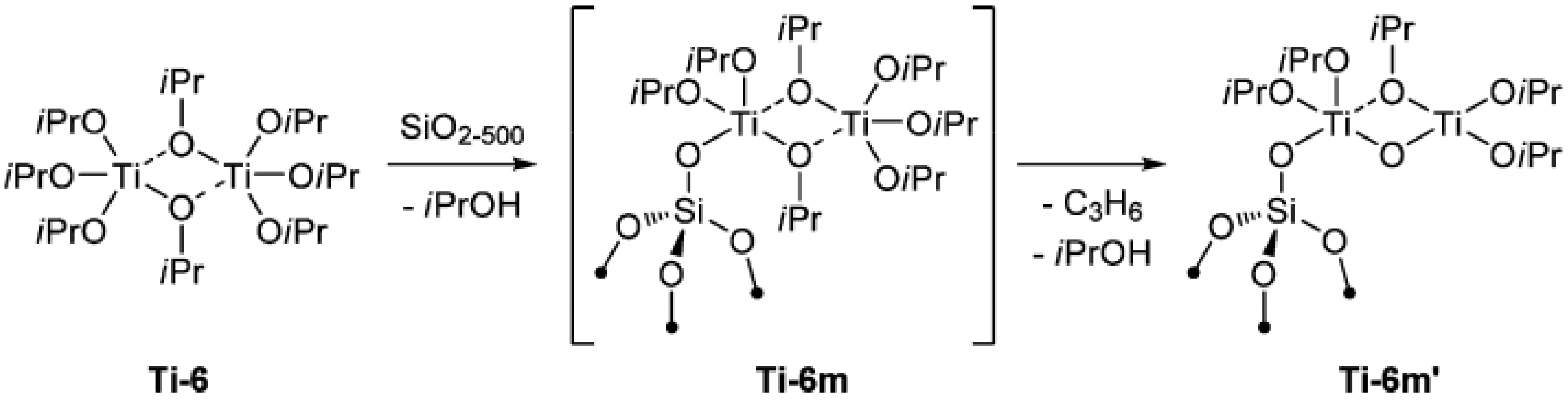
Surface Organometallic and Coordination Chemistry toward Single-Site Heterogeneous Catalysts: Strategies, Methods, Structures, and Activities

Christophe Copéret,[*,†] Aleix Comas-Vives,[†] Matthew P. Conley,[†] Deven P. Estes,[†] Alexey Fedorov,[†] Victor Mougel,[†] Haruki Nagae,[†,‡] Francisco Núñez-Zarur,[†] and Pavel A. Zhizhko[†,§]

Single site catalysts

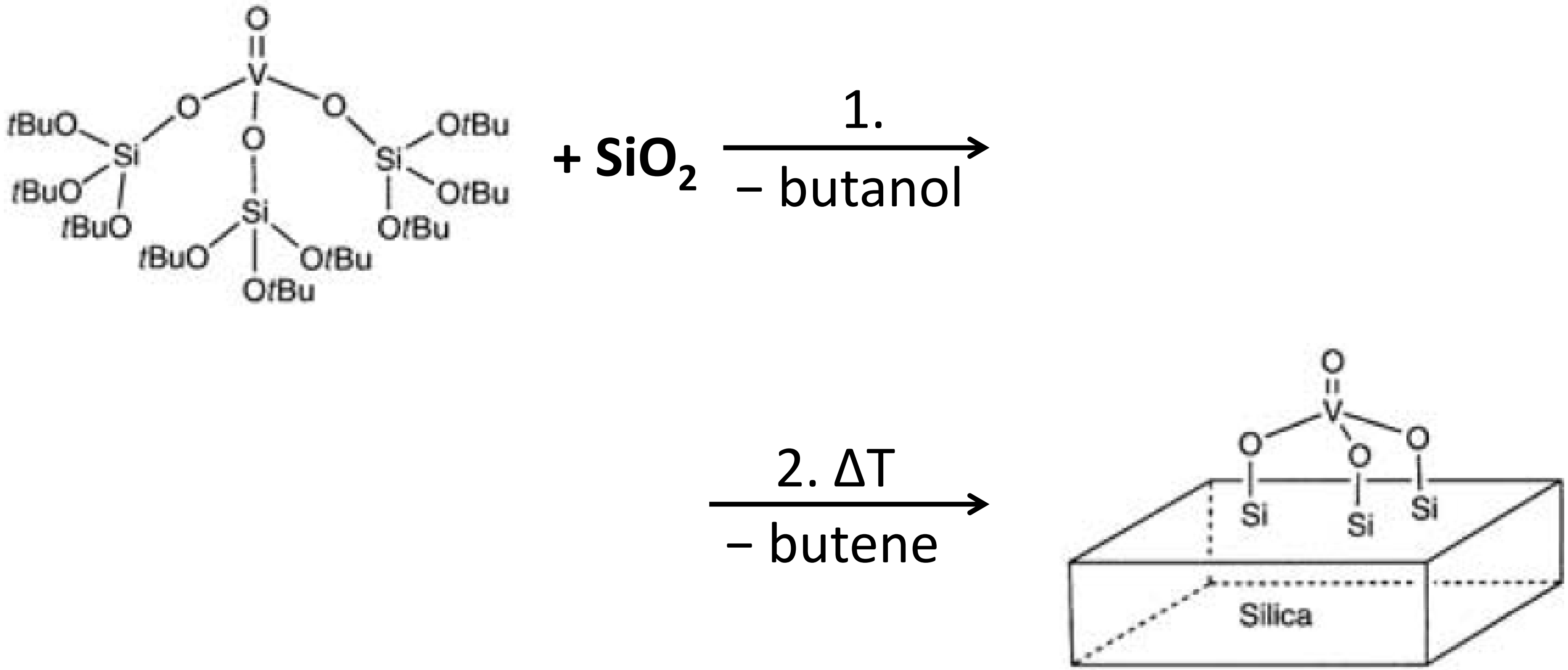






Single site catalysts

- In many cases silica needed all around the active site (no unreacted chlorines etc.)

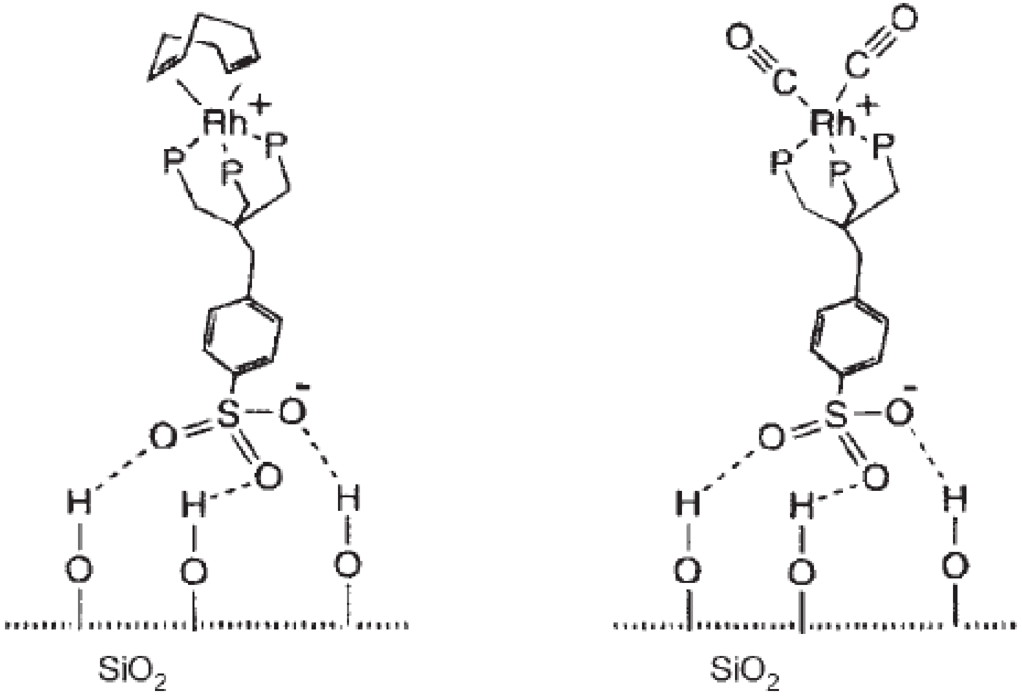


+ SiO_2 $\xrightarrow[-\text{ butanol}]{1.}$

$\xrightarrow[-\text{ butene}]{2.\ \Delta T}$

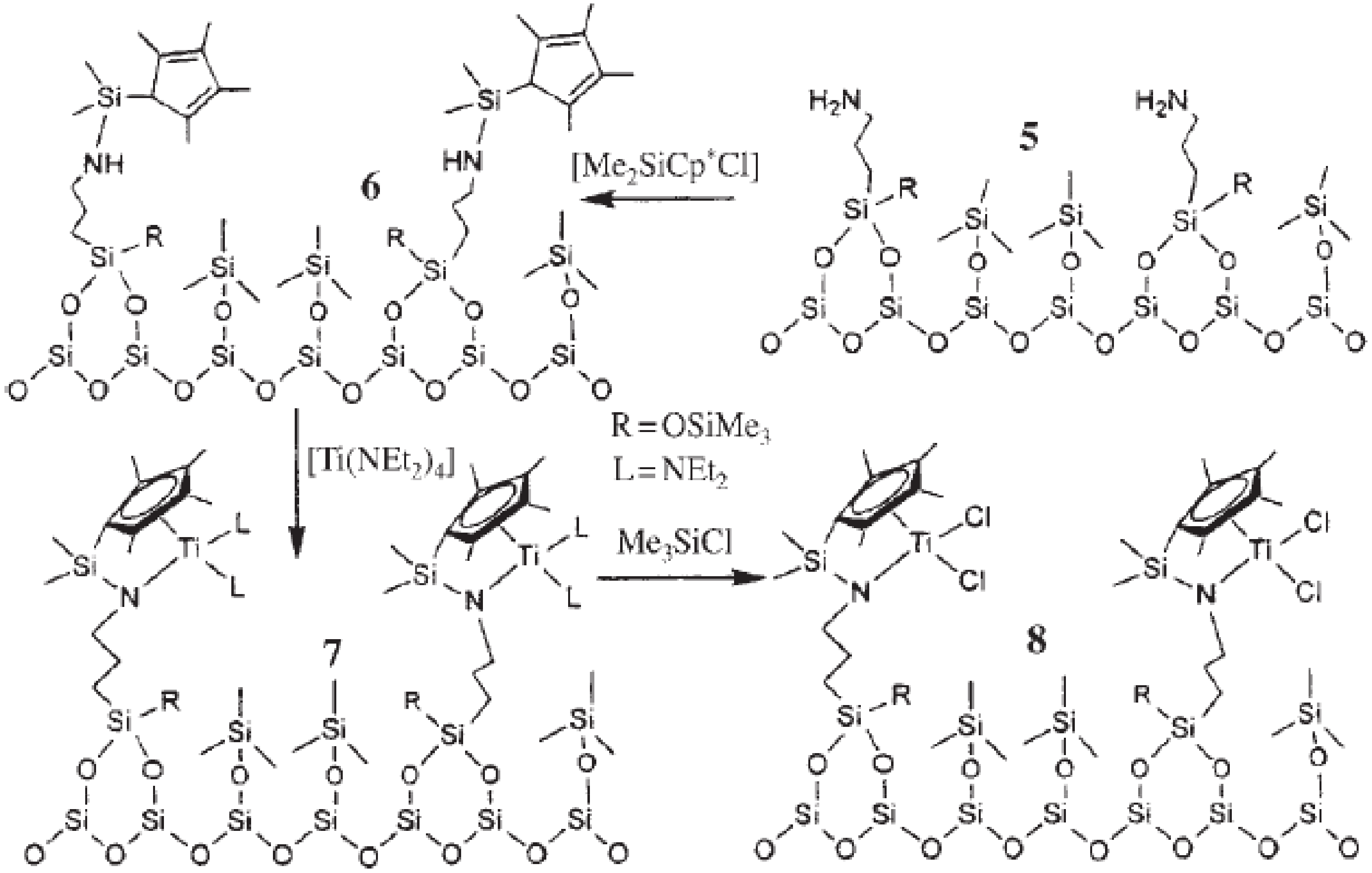
Single site catalysts

- Grafting on silica – other types of bonding



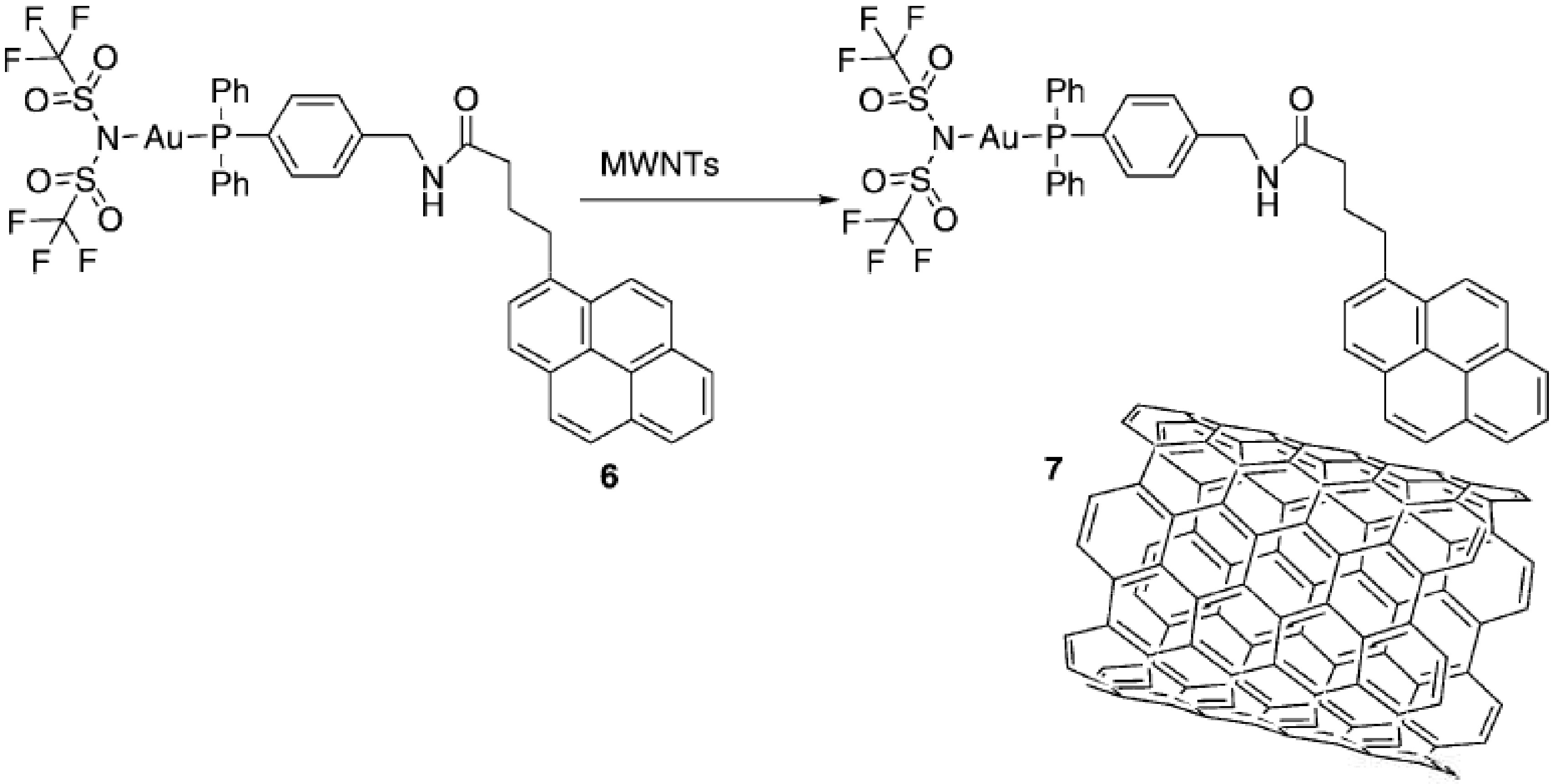
Single site catalysts

- Grafting on silica – other types of bonding



Single site catalysts

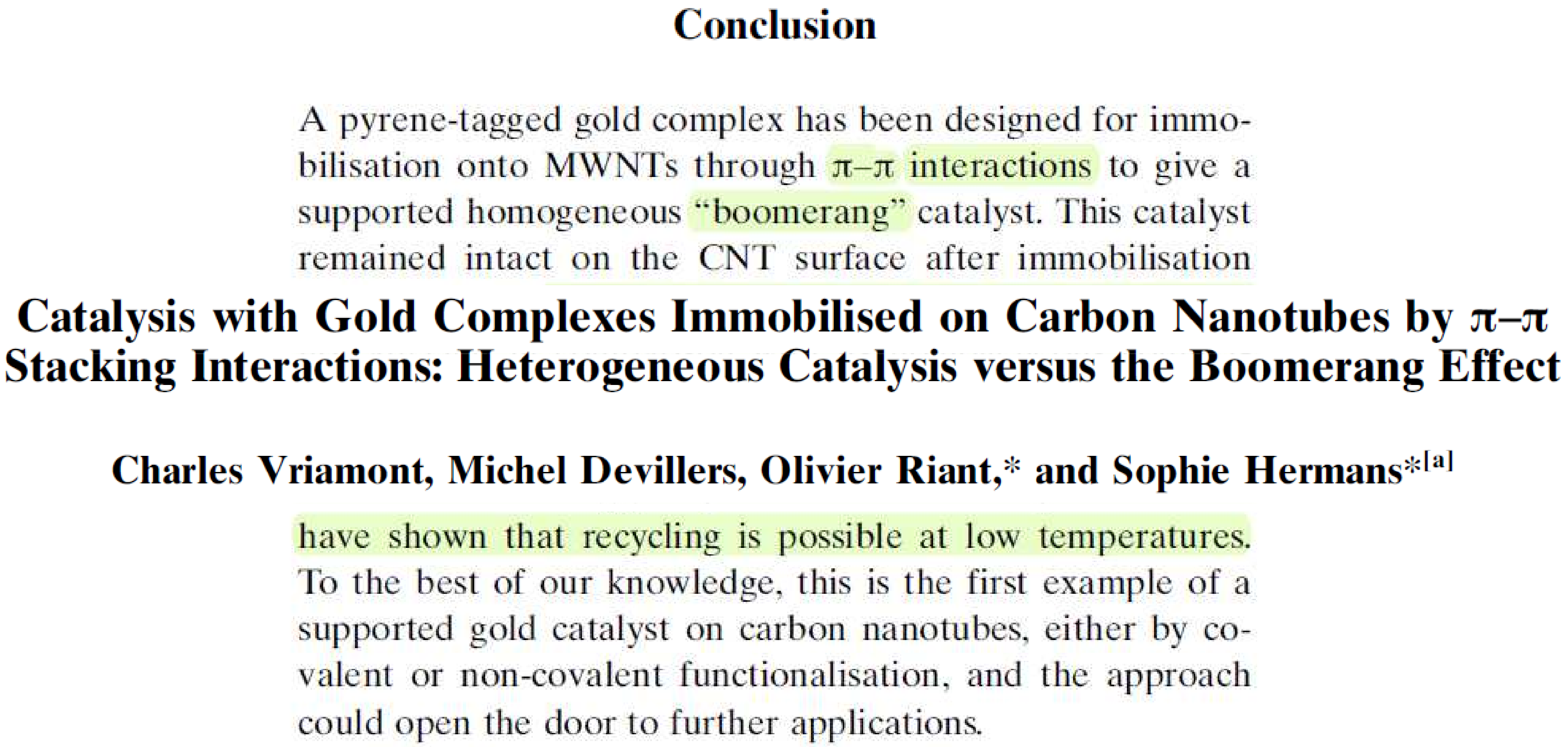
- Grafting on carbon – π-π stacking



Scheme 3. Incorporation of the pyrene-tagged gold complex **6** onto MWNTs.

Single site catalysts

- Grafting on carbon – π-π stacking
  - Boomerang effect



Conclusion

A pyrene-tagged gold complex has been designed for immobilisation onto MWNTs through π–π interactions to give a supported homogeneous "boomerang" catalyst. This catalyst remained intact on the CNT surface after immobilisation have shown that recycling is possible at low temperatures. To the best of our knowledge, this is the first example of a supported gold catalyst on carbon nanotubes, either by covalent or non-covalent functionalisation, and the approach could open the door to further applications.

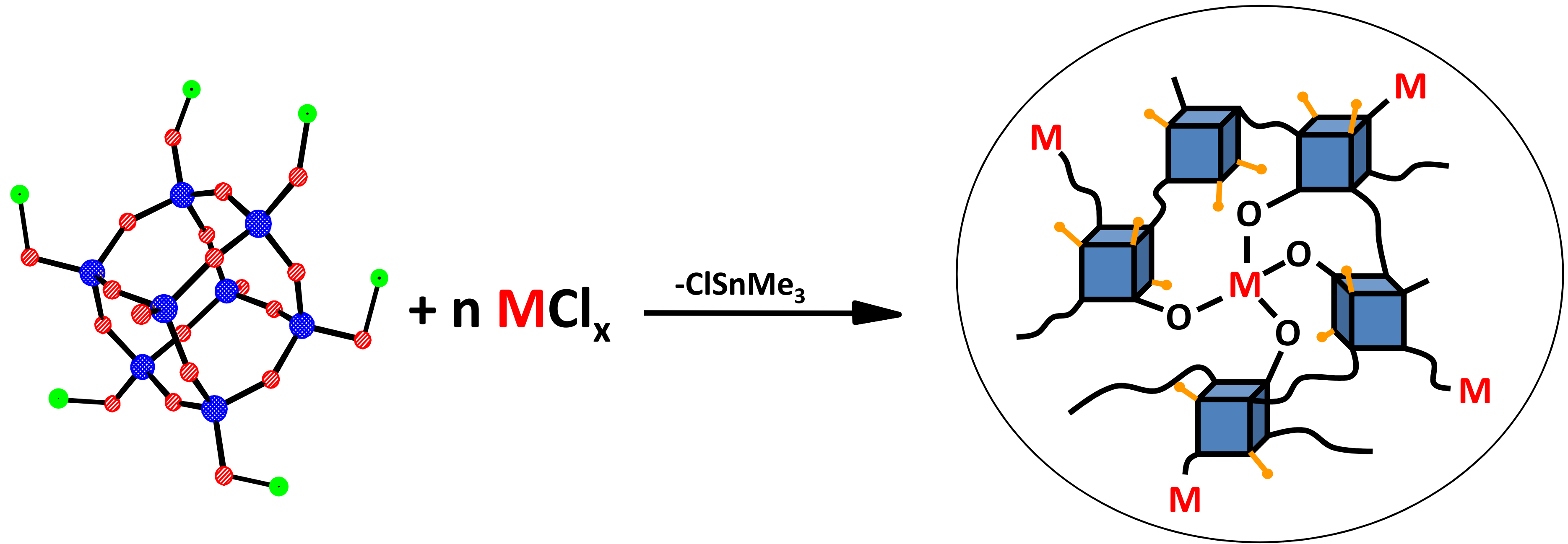
Catalysis with Gold Complexes Immobilised on Carbon Nanotubes by π–π Stacking Interactions: Heterogeneous Catalysis versus the Boomerang Effect

Charles Vriamont, Michel Devillers, Olivier Riant,* and Sophie Hermans*[a]

Single site catalysts

- What is it?
  - **Individual isolated ion/atom/molecular complex/cluster**
    - Grafted on porous support
    - **Created within the material by building block approach**
  - „Ship in bottle“ structures– e.g. molecular complex/enzyme trapped within a zeolitic cage
  - Crystalline, open-structure, microporous solids (e.g. zeolites) with active sites uniformly distributed throughout the bulk

Single site catalysts



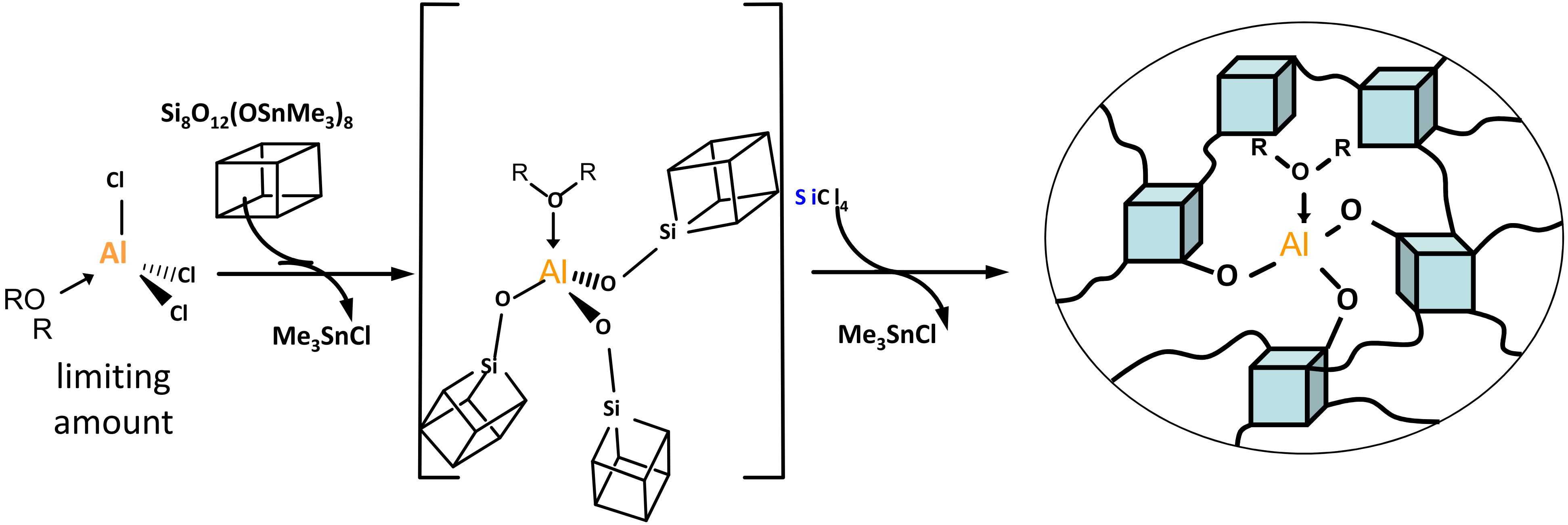
$Si_8O_{20}(SnMe_3)_8$

● = **$SnMe_3$**

MCl_x = PCl_3, $SiCl_4$, BBr_3, $AlCl_3$, $GaCl_3$, $TiCl_4$, $ZrCl_4$, VCl_4, $VOCl_3$, $SnCl_4$, WCl_6, MoO_2Cl_2

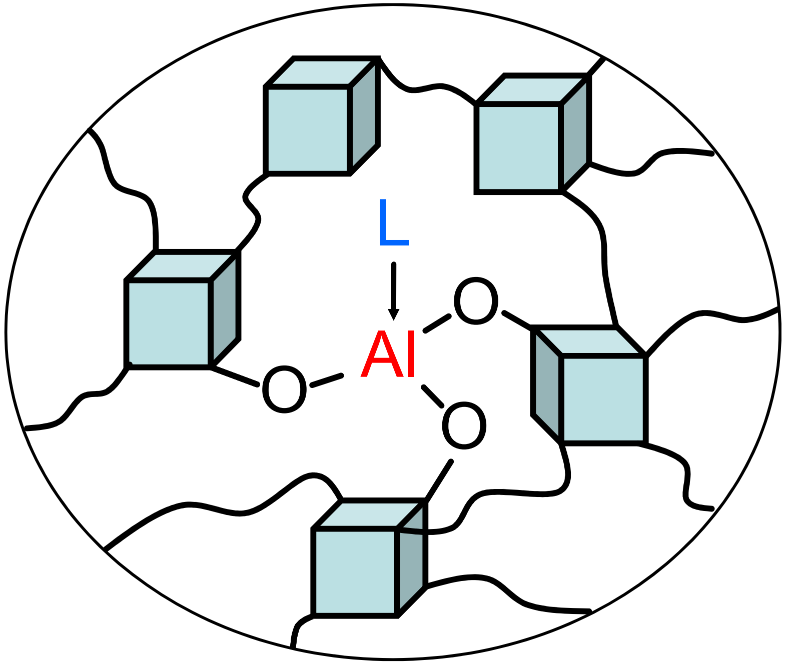
1. N.N. Ghosh, J.C. Clark, G.T. Eldridge, C.E. Barnes, Chem. Comm., (2004) 856-857.
2. M.-Y. Lee, J. Jiao, R. Mayes, E. Hagaman, C.E. Barnes, Catalysis Today, 160 (2011) 153-164.

Single site catalysts

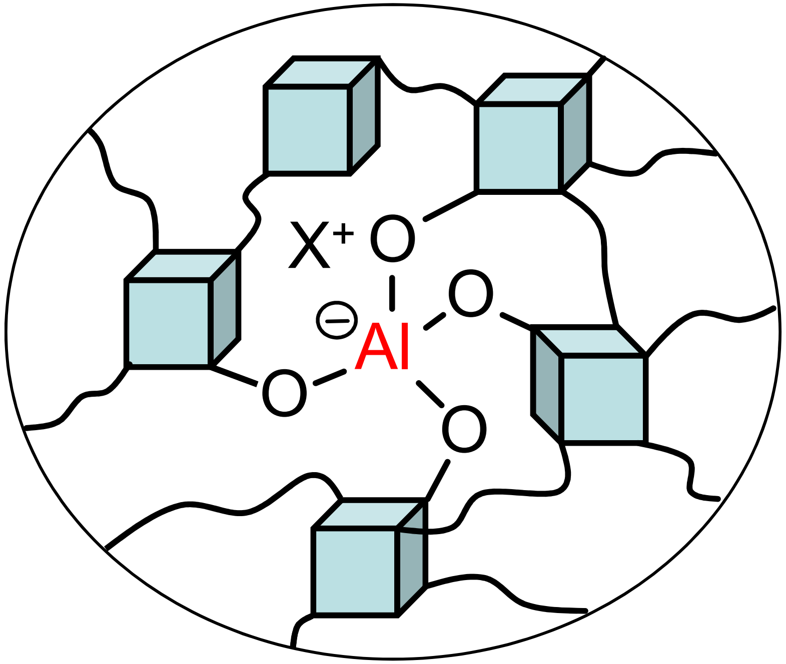


Single site catalysts

- Targeting connectivity



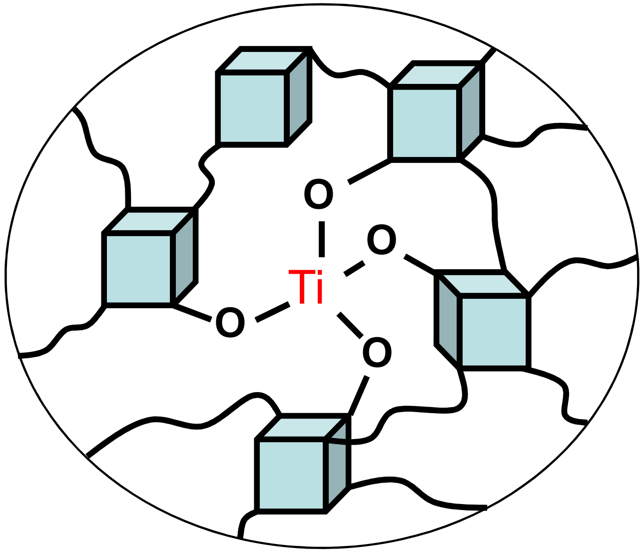
3C-Al←L
L = py (1), THF (2)



[X][4C-Al]
X = NBu_4^+ (3)

Single site catalysts

- Targeting geometry
  - Tetrahedral
  - Square planar



4C-Ti

Single site catalysts

- What is it?
  - **Individual isolated ion/atom/molecular complex/cluster**
    - **Grafted on porous support**
    - **Created within the material by building block approach**

    CHARACTERIZATION?
  - „Ship in bottle“ structures– e.g. molecular complex/enzyme trapped within a zeolitic cage
  - Crystalline, open-structure, microporous solids (e.g. zeolites) with active sites uniformly distributed throughout the bulk

Single site catalysts

- EXAFS + XANES

Single site catalysts

- What is it?
  - Individual isolated ion/atom/molecular complex/cluster
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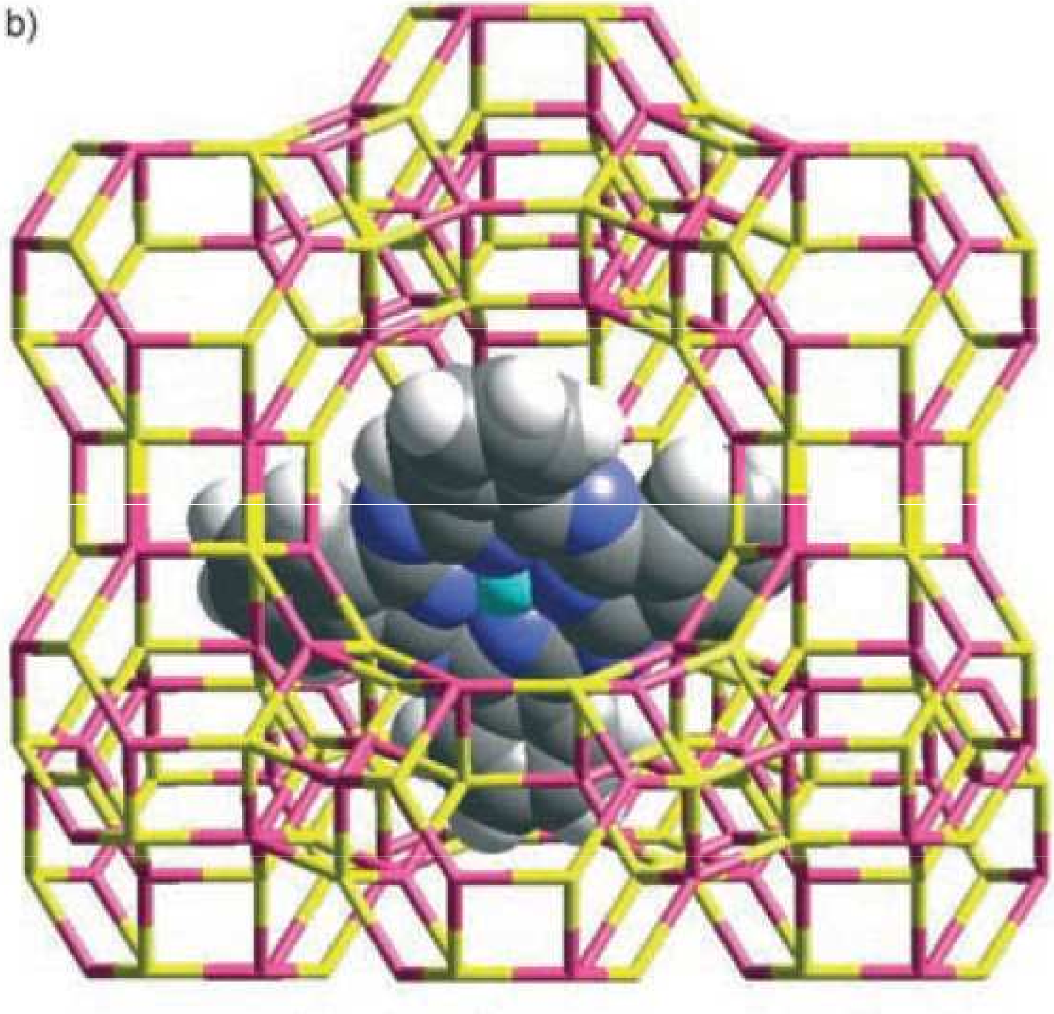
    - Created within the material by building block approach
  - **„Ship in bottle“ structures– e.g. molecular complex/enzyme trapped within a zeolitic cage**
  - Crystalline, open-structure, microporous solids (e.g. zeolites) with active sites uniformly distributed throughout the bulk

Single site catalysts



Cobalt phthalocyanine within zeolite Y

Single site catalysts

- Single site very well preserved (no dimerization,…)
- Diffusion of molecules small enough in the micropore system of zeolite – both reactants and products – enhancing specificity and selectivity

Single site catalysts

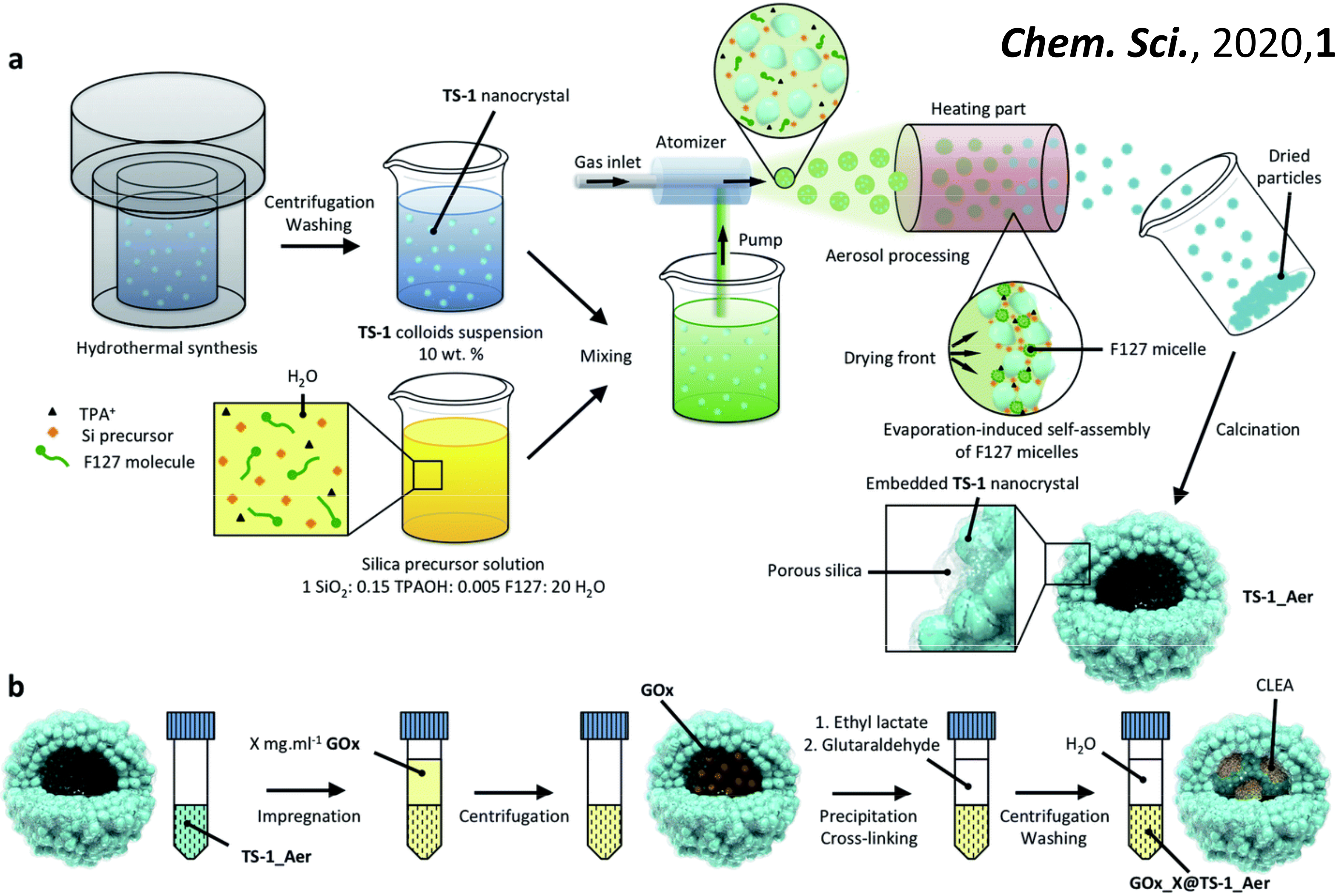
- Synthesis?
  - Cation exchange (2Na^+ for Co^{2+})
  - Complexation with ligands within the zeolite pores

„Co^{2+}-exchanged zeolite-Y was heated with excess amount of 1,2-dicyanobenzene (DCB) under vacuum. Excessive DCB was then extracted (Soxhlet).
The dicyanobenzene molecule is small enough (∼6.5 Å) to diffuse through the 7.4 Å windows of the supercage of the zeolite and condense around the metal ion to form cobalt phthalocyanine.“

Single site catalysts

- Enzyme agglomerates inside a hollow silica sphere

Chem. Sci., 2020,**11**, 954-961



Single site catalysts

- What is it?
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  - „Ship in bottle“ structures– e.g. molecular complex/enzyme trapped within a zeolitic cage
  - **Crystalline, open-structure, microporous solids (e.g. zeolites) with active sites uniformly distributed throughout the bulk**

Single site catalysts

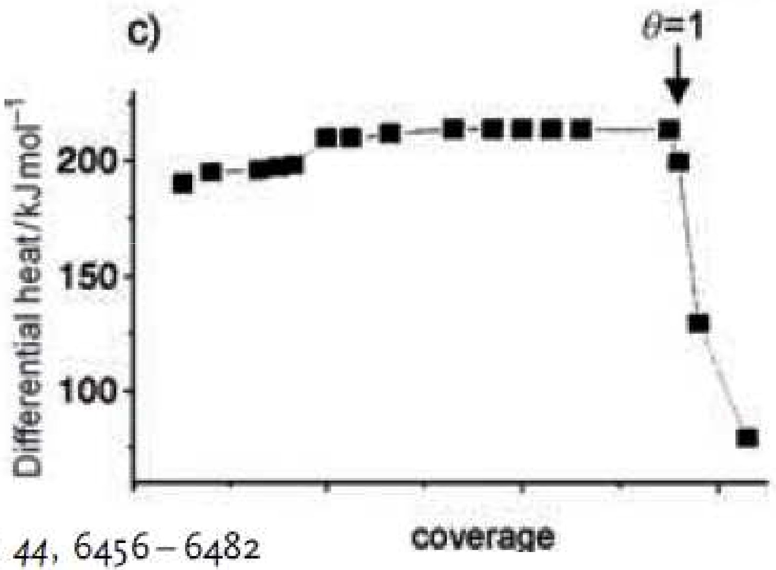
- Zeolites
  - ≡Si−O(H)−Al≡
- MAlPOs
  - $\equiv M^{II}$−O(H)−P≡
  - M = Mg, Co, Zn, Mn…

Single site catalysts

- Zeolites and MAlPOs
  - Microporous
  - Crystalline
  - Ideal to study by many analytical techniques

Single site catalysts

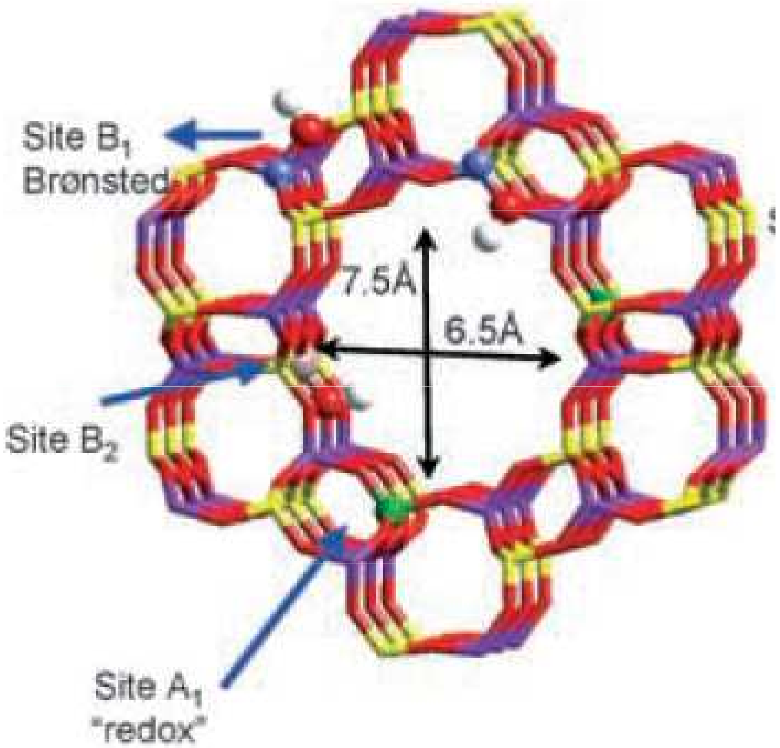
- Zeolites and MAlPOs
  - Isolated sites???
    - Si/Al ratio ≥ 200; perfect crystallinity
  - Equivalent sites???
  - Amorphous grains/surface species



Angew. Chem. Int. Ed. **2005**, 44, 6456–6482

Single site catalysts

- Zeolites and MAlPOs
  - Isolated sites???
  - Equivalent sites???
    - Different positions in cage
  - Amorphous grains/surface species



Single site catalysts

- Zeolites and MAlPOs
  - Isolated sites???
  - Equivalent sites???
  - Amorphous grains/surface species
    - e.g. extraframework aluminum species
      - From not fully embedded (connectivity = 3) surface Al atoms to amorphous alumina (nano)particles
      - **Tetra**, penta, hexacoordinated
      - Easy to overlook (99 % of the material is crystalline), but important to notice
      - Their role in catalysis???

Single site catalysts

- Similar but different (Markus Antoinetti et al.)

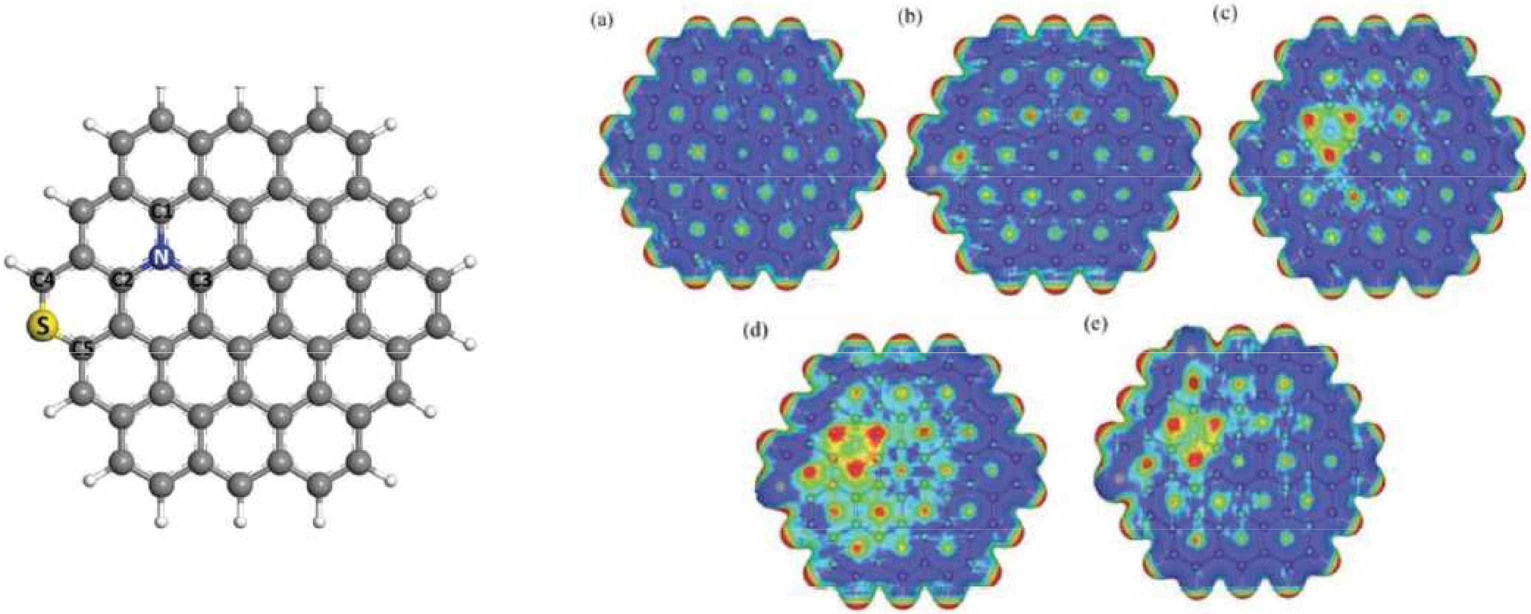
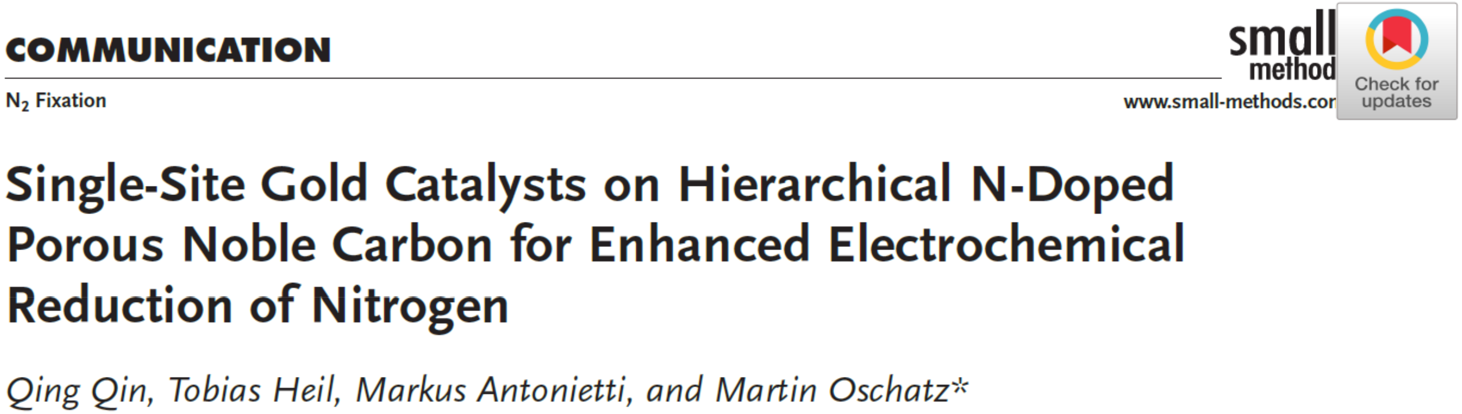


Figure 7. Molecular model of S,N dual-doped graphene and electrostatic potential mapping from charge density matrix for: a) nondoped model graphene, b) S–G, c) N–G, d) S–N-G, and e) S–S–N–G. Reproduced with permission.[117] Copyright 2015, Wiley-VCH.

- Doped graphene sheets
- Isolated sites located by HR-TEM

Single site catalysts

- Doped graphene sheets
  - Single **metal** atoms within carbon layer
    - Single atom = „complex like“
    - Conductive carbon layer, electrons shared = „metal like“
    - **Unique**
    - Single-site Au highly active in Haber-Bosch ammonia synthesis, mild conditions



COMMUNICATION

small method

N_2 Fixation

www.small-methods.cor

Check for updates

Single-Site Gold Catalysts on Hierarchical N-Doped Porous Noble Carbon for Enhanced Electrochemical Reduction of Nitrogen

*Qing Qin, Tobias Heil, Markus Antonietti, and Martin Oschatz**

Single site catalysts

- Doped graphene sheets
  - Single **Au** atoms within N-doped graphene

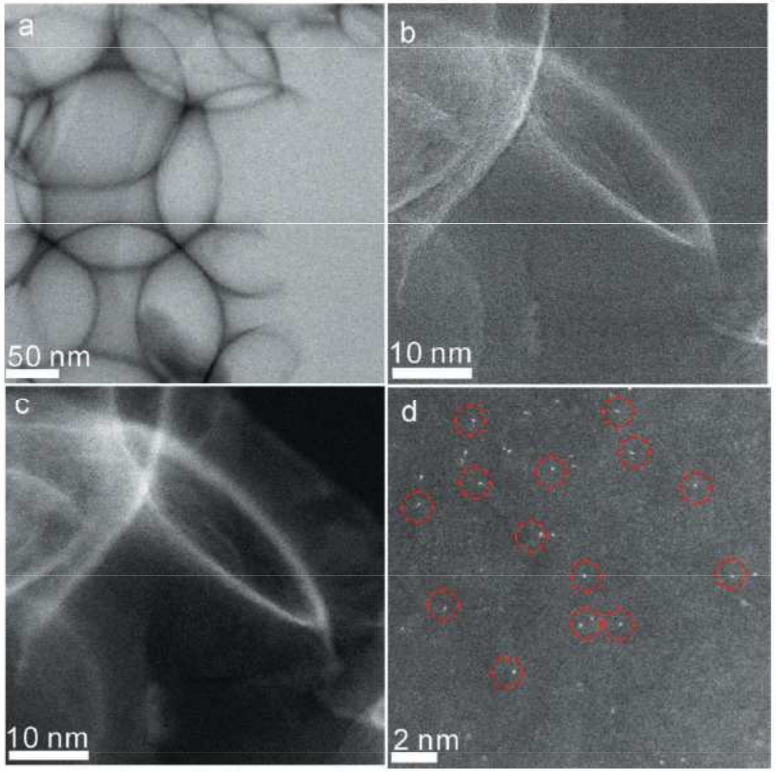
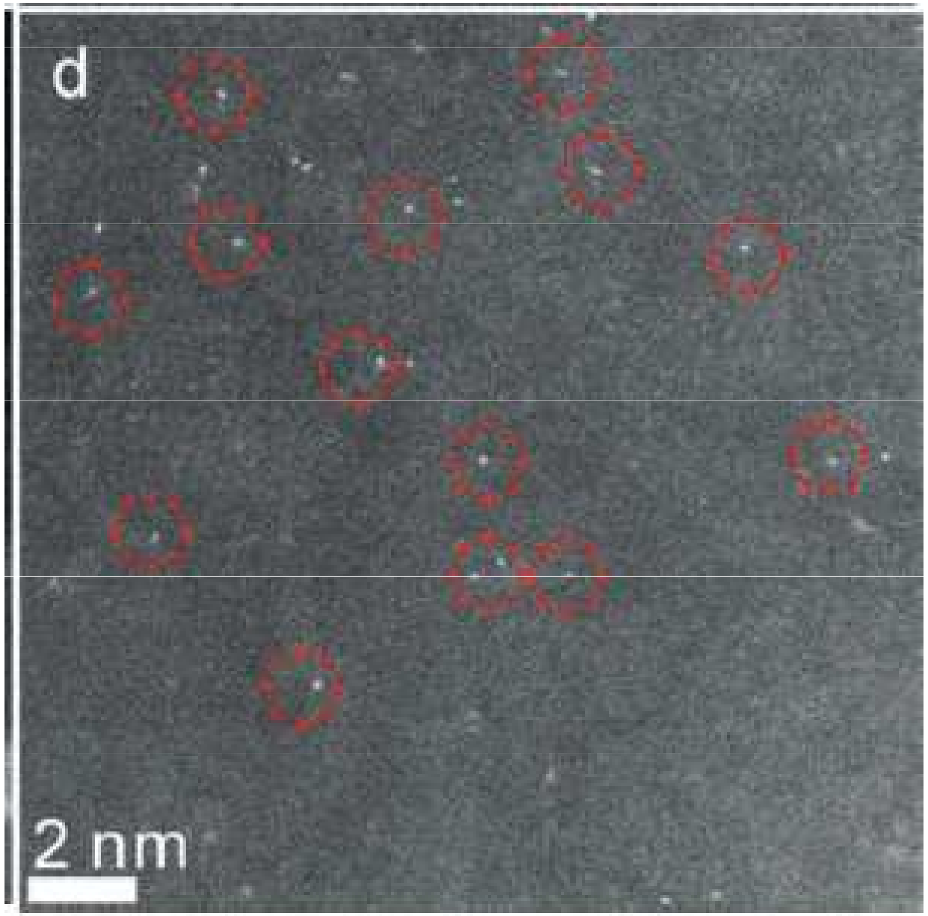
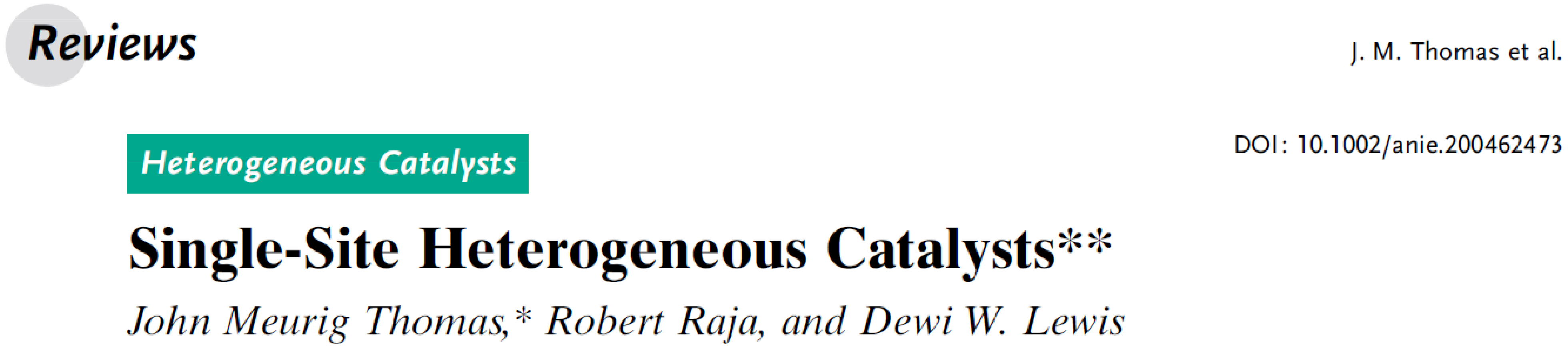


Figure 1. a) Representative TEM image of AuSAs-NDPCs. b) Aberration-corrected STEM image in bright-field mode. c) Aberration-corrected STEM image in dark-field mode. d) High-magnification HAADF-STEM image, showing that only Au single species is present.



References


Reviews

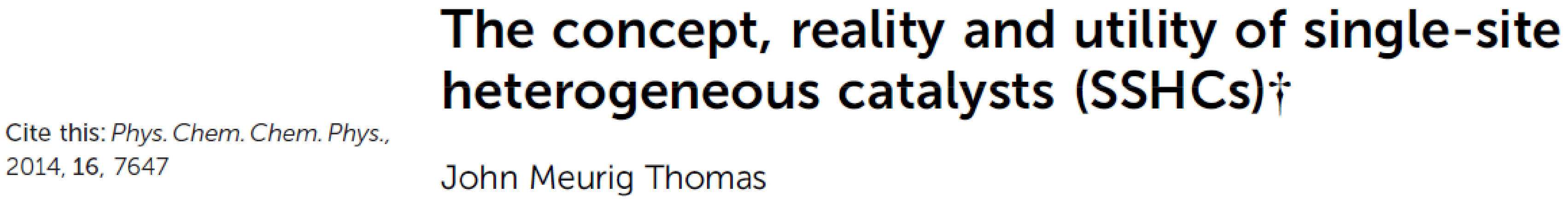
J. M. Thomas et al.

Heterogeneous Catalysts

DOI: 10.1002/anie.200462473

Single-Site Heterogeneous Catalysts**

John Meurig Thomas, Robert Raja, and Dewi W. Lewis*


Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 7647

The concept, reality and utility of single-site heterogeneous catalysts (SSHCs)†

John Meurig Thomas