NanoSim: A Multi-scale Simulation Based Design Platform for Cost-Effective CO_2 Capture Processes using Nano-Structured Materials

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SINTEF

- Independent research institute for applied science and technology
- 2000 employees (Norway, Denmark, Brazil, USA)
- Motto: "Technology for a better society"
- Close connections to both industry and academia
- Well integrated with universities in Trondheim and Oslo
- Funding: 7% basic funding, 40% industry, competitive grants (Norway, EU)
- Fields of research
  - **Oil and gas (multi-phase flow, enhanced oil recovery)**
  - **Metallurgy (silicon, manganese, aluminium,…)**
  - **Marine technology and aquaculture (fisheries)**
  - Materials science and engineering
  - CO_2 capture
  - Biotechnology
  - Catalysis
  - Energy technologies (solar cells, batteries, wind,…)
  - Computational science and engineering
  - Construction engineering
  - Civil engineering
  - Medical technology
  - Social sciences (health, economics, safety)

"Atomic-scale modeling" staff@SINTEF (Trondheim and Oslo)

- Materials science
- Metallurgy
- Catalysis
- CO_2 capture
- Hydrogen storage
- Solar cells
- Thermoelectric materials
- Combustion
- …

- Multiscale modeling
  - Kinetics
  - Thermodynamics
  - Fluid dynamics
  - Finite element
  - …


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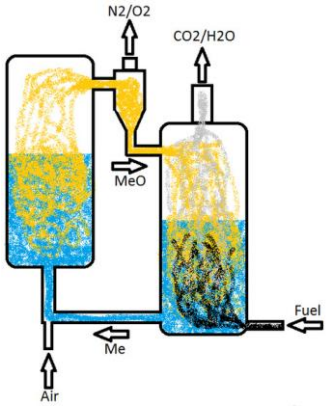
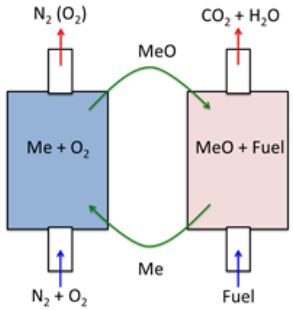
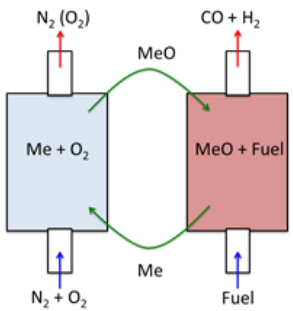
NanoSim

- EU FP7 grant (2014-2017) (http://www.sintef.no/projectweb/nanosim/)
- **Simulation-based design** of reactive particles for Chemical Looping Combustion (CLC) and Chemical Looping Reforming (CLR) for power, fuel or chemicals generation with **integrated CO_2 capture**
- Idea: Embed **reactive nanoparticles** (oxygen carrier) in inert porous micron-sized particles to increase reactivity and stability

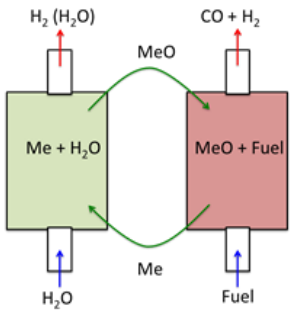




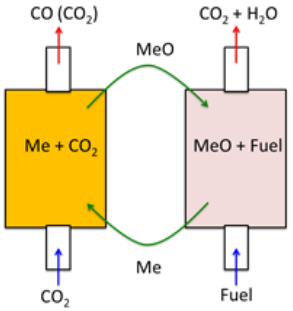
CLC



CLR



CLSR



CLDR

NanoSim

Main objectives

- Develop an **open-source computational platform** that will allow the rational design of the second generation of **gas-particle CO_2 capture** technologies based on **nano-structured materials**
- **Design** and manufacture **nano-structured materials** and shorten the development process of nano-enabled products based on the multi-scale modelling
- **Design** and demonstrate an **energy conversion reactor** with CO_2 capture based on the superior performance of nano-structured materials

NanoSim

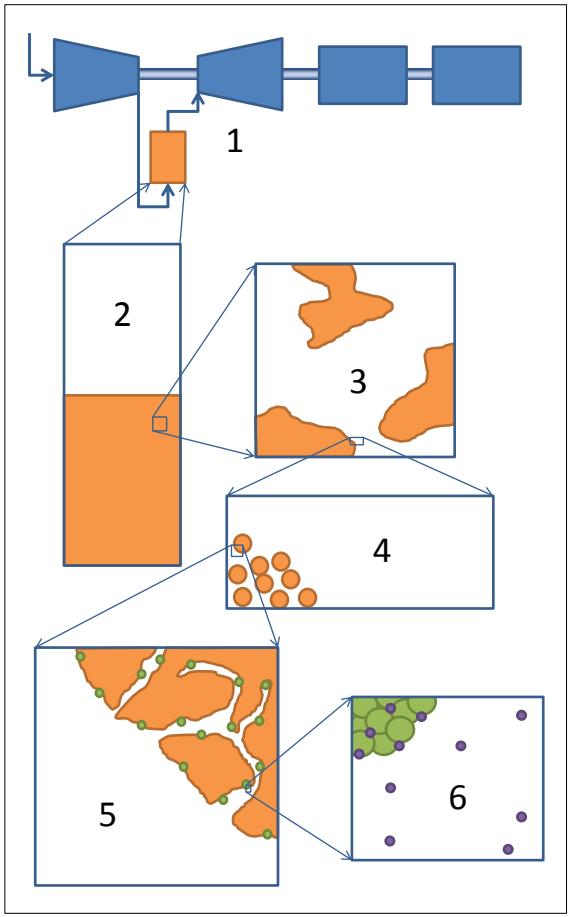
Specific objectives

- Develop an **integrated multi-scale modelling platform** through connection and incorporation of a variety of models at different scales
- Advance the modelling state of the art at each particular scale to ensure accurate simulation of relevant large-scale processes
- **Experimentally validate models** developed at the five defined scales
- **Reduce the time spent on materials development by 50%** compared to traditional approaches
- Enable and accelerate the rational development of CO_2 capture processes

NanoSim

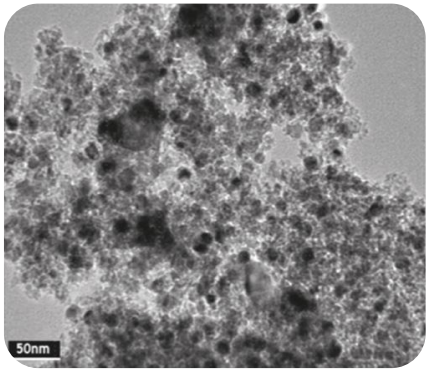
1. Process scale: Techno-economic evaluation
2. Equipment scale: 1D phenomenological model
3. Cluster scale: CFD (Eulerian)
4. Particle scale: CFD (Lagrangian)
5. Intra-particle scale: Mass+heat transport, kinetics
6. Atomic scale: DFT, Kinetic Monte Carlo

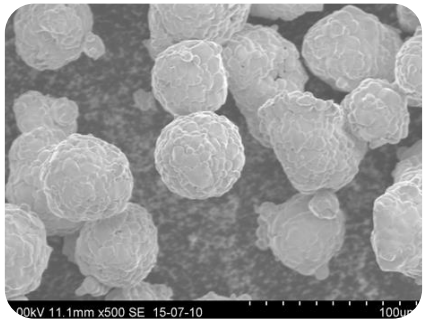
- Experiments: synthesis and test reactor
- Common data handling structure
- Direct coupling of scales 4 and 5

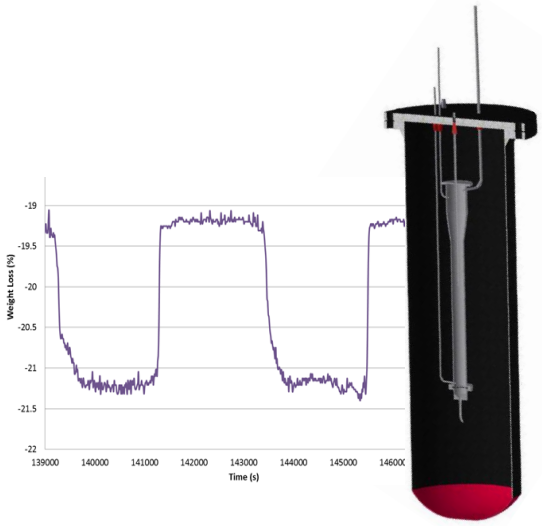


Interaction between atomic-scale and intra-particle scale and experiments

Experimental validation (SINTEF)







Synthesis of stabilised nanoparticles

- Selected OC material in suitable, inert, porous matrix material
- Provides thermal stability and suitable oxygen carrying properties

Impregnation on support

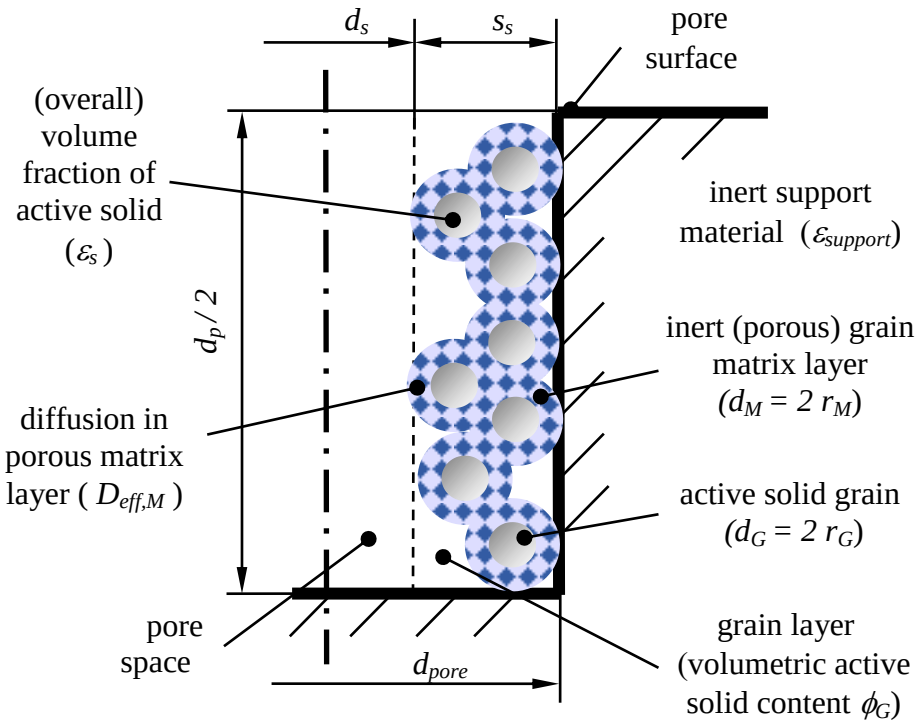
- Provides mechanical strength and suitable flow properties

Experimental validation

- Thermogravimetric redox testing (capacity and kinetics)
- Lab-scale reactor testing
- Provides experimental data to be evaluated against predictions from the NanoSim platform

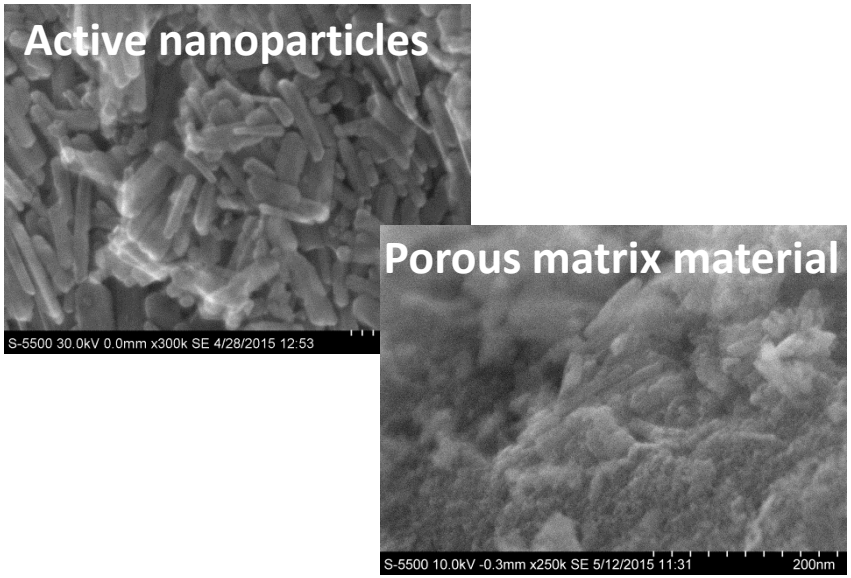
Modelling (TU Graz)

- Sensitivity analysis with particle-scale model to predict nanostructured particle parameters



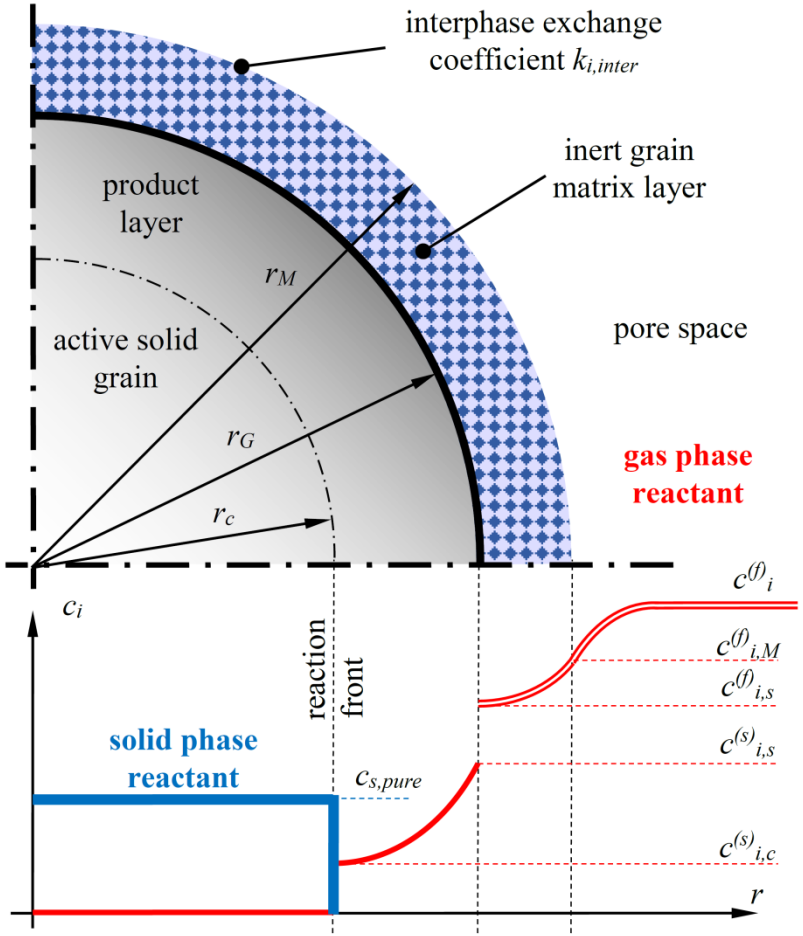
Experimental validation

- Synthesis of nano-structured oxygen carriers



- Spectroscopic studies of real structures and kinetic properties of these provide input to modelling

Model of reacting nanoparticle



- Diffusion of fuel through porous inert material
- Reaction of fuel with nanoparticle
- Diffusion of fuel through product layer and/or diffusion between solid reactant and product

Oxygen carriers for chemical looping technologies

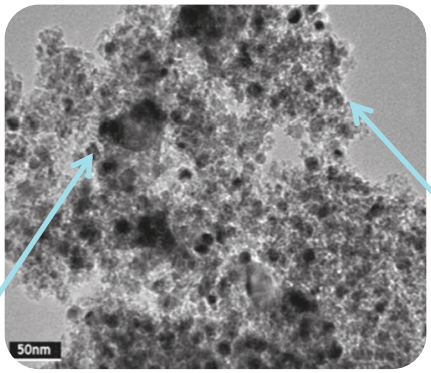
- …should ideally have these qualities:
  - **High oxygen carrying capacity**
  - **Fast kinetics of oxidation and reduction** under the desired process conditions
  - Enable the **desired degree of fuel combustion** (full or partial, depending on the process)
  - **Chemically stable** under **repeated redox cycling** at the process temperature
  - Spherically shaped, and with **good fluidisation characteristics** (for **fluidised bed**-type reactors)
  - Robust and resistant against attrition and segmentation
  - **No agglomeration of particles** under process conditions
  - Resistive to carbon deposition during the reduction step
  - Low-cost
  - Based on material which is available all over the world
  - Based on a simple production process
  - **Non-hazardous** for humans and environment

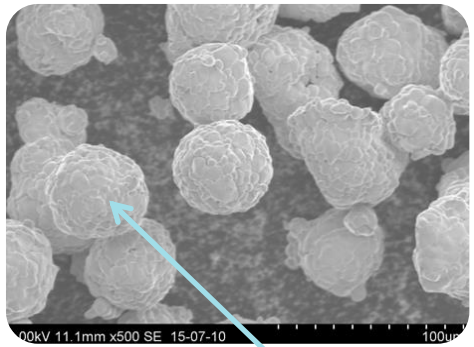
Some important criteria

OC couple	*Max OC capacity*	*Toxicity*	*TM*	*Reactivity*
NiO/Ni	13.63	High	1455	Good
CuO/Cu	12.59	Low	1085	Good
Cu2O/Cu	6.29	Low	1085	Good
Fe2O3/Fe3O4	0.19	Low	1597	Medium
Fe2O3/FeO	5.57	Low	1360	Medium
Fe3O4/FeO	3.79	Low	1360	Medium
Mn2O3/MnO	5.64	Low	1650	Medium
Mn3O4/MnO	3.83	Low	1650	Medium
Co3O4/Co	18.19	High	1495	(unknown)
CoO/Co	13.58	High	1495	(unknown)

- Ni and Co are excluded due to high toxicity (which is greatly enhanced for nanomaterials)
- Cu is excluded due to a low melting temperature, which will also give a high reactivity towards the support

Thermodynamic screening – candidate materials





- **Oxygen Carriers (OC)**:
- $Fe/FeO/Fe_3O_4/Fe_2O_3$
- $Mn/MnO/Mn_3O_4/Mn_2O_3$

- Good oxygen carrying capacity
- Affordable
- Environmentally friendly
- Suitable melting temperature

- **Support material 1**:
- $BaAl_{12}O_{19}$
- $SrAl_{12}O_{19}$
- $LaAl_{11}O_{18}$
- $LaMgAlO_{19}$

- Should thermally stabilise OC
- High thermal stability
- Promising stability towards OC and Support 2

- **Support material 2**:
- Al_2O_3

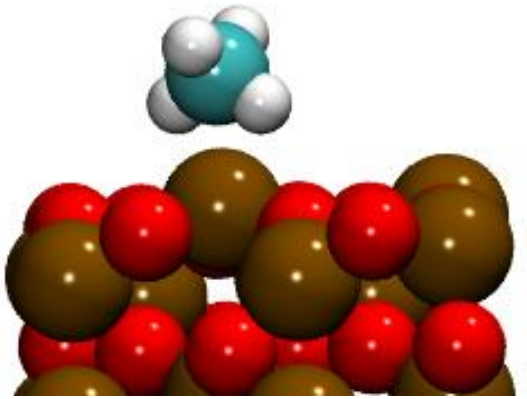
- Commercially available in variety of morphologies
- Thermally stable
- High mechanical strength
- Promising stability towards Support 2

Atomic-scale modelling (UCL and SINTEF)

- DFT (VASP)
- Transition state theory (elementary reaction and diffusion steps)
- Kinetic Monte Carlo (overall reaction kinetics)
- New set of scripts: **REMARC** (REaction Mechanism And Rate Calculator)
  - Smoothly translates DFT data to kinetics and thermodynamics for set of reactions
  - Output: direct input for Kinetic Monte Carlo and rate equation models (CHEMKIN/Surface CHEMKIN) and reaction thermodynamics
- **Objectives**: provide input for particle-scale models, interpretation of experiments, and design of oxygen carrier particles
- **First test system:**
  - Fuel: **CH_4**
  - Oxygen carrier system: **Fe_2O_3 / Fe_3O_4 / FeO**

NanoSim

- **Modelling Surface Processes occurring during Chemical Loop Reforming of Methane catalysed by Fe-oxides: A first-principles approach**



UCL

Fe_2O_3: Elementary Reaction Steps

$$CH_{4(g)} \rightarrow CH_{4(ads)}$$

$$CH_{4(ads)} \rightarrow CH_{3(ads)} + H_{(ads)}$$

$$CH_{3(ads)} \rightarrow CH_{2(ads)} + H_{(ads)}$$

$$CH_{2(ads)} \rightarrow CH_{(ads)} + H_{(ads)}$$

$$CH_{(ads)} \rightarrow C_{(ads)} + H_{(ads)}$$

$$CH_{(ads)} + O_{(ads)} \rightarrow CHO_{(ads)}$$

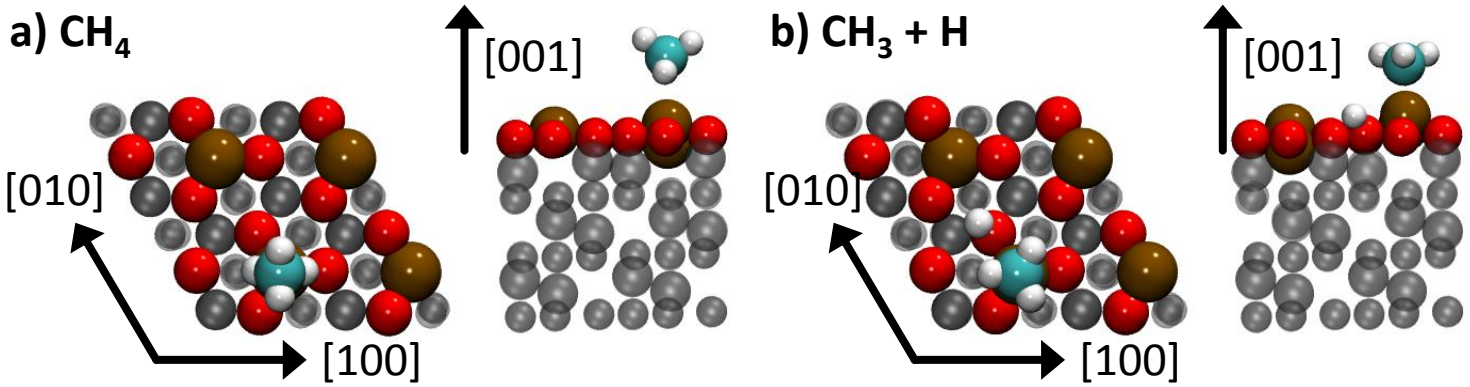
$$CHO_{(ads)} \rightarrow CO_{(ads)} + H_{(ads)}$$

- Majority of literature suggests CLR reaction pathway proceeds via CHO radical[1].
- Final Step: $\mathbf{2CHO_{(ads)} \rightarrow 2CO_{(ads)} + H_{2(g)}}$
- Other possible adsorbed species:
  - H_2O
  - OH

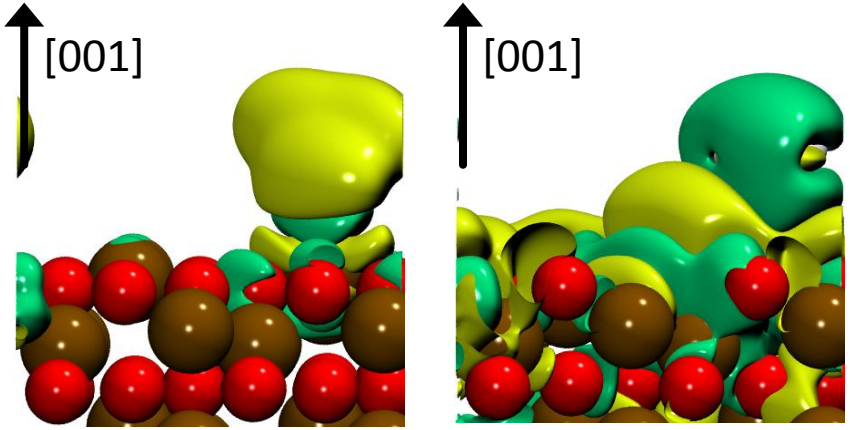
[1] M. Wang *et al.*, *Fuel*, 2014

Fe_2O_3: Step 1

- Optimised geometries for CH_4 and CH_3+H



- Electron density transferred from adsorbates to surface for dissociated state (CH_3+H).



a) CH_4 b) CH_3 + H

Fe_2O_3: Step 1

Free energies of both associative and dissociative adsorption predicted to be unfavourable for T> 0K.

$\Delta G_{bind}(T)^{CH4}$: $CH_{4(g)} \rightarrow CH_{4(ads)}$

$\Delta G_{bind}(T)^{CH3+H}$: $CH_{4(g)} \rightarrow CH_{3(ads)} + H_{(ads)}$

T /K	$\Delta G_{bind}(T)^{CH4}$ /kJ mol^{-1}	$\Delta G_{bind}(T)^{CH3+H}$ /kJ mol^{-1}
0	-7.8	+7.6
773	+166.7	+205.7
873	+188.9	+230.9
1173	+254.3	+305.4

T /K	$\Delta G_r(T)^{gas}$ /kJ mol^{-1}	$\Delta G_r(T)^{surf}$ /kJ mol^{-1}
0	+421.1	+15.4
773	+333.6	+30.9
873	+320.3	+42.0
1173	+279.5	+51.0

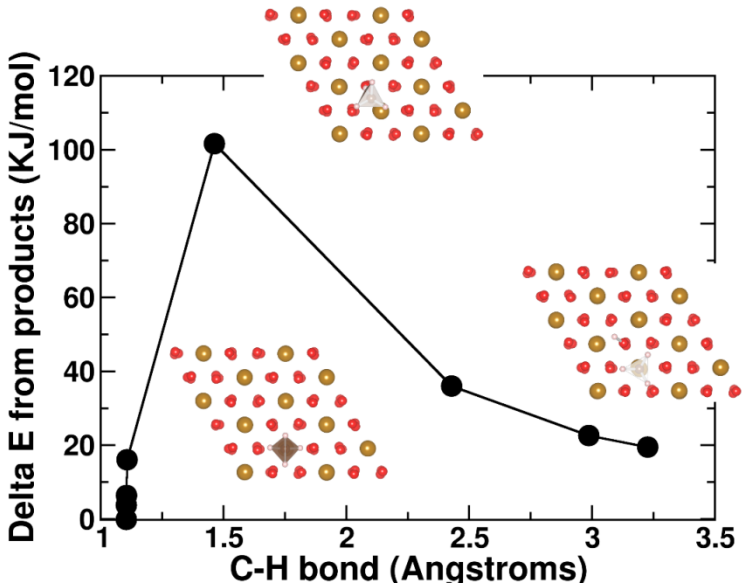
First step of CH_4 dissociation is thermodynamically more favourable in the presence of (0001) Fe_2O_3 than in gas phase.

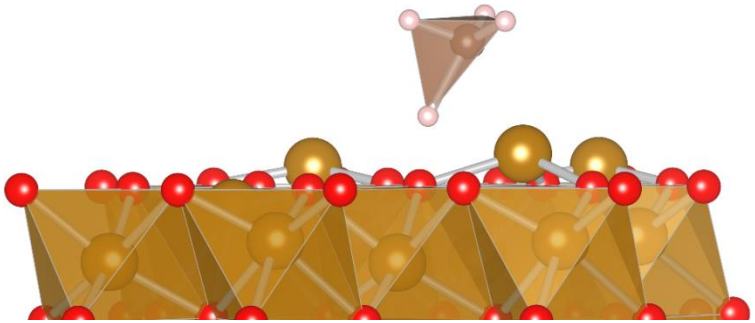
$\Delta G_r(T)^{gas}$: $CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$

$\Delta G_r(T)^{surf}$: $CH_{4(ads)} \rightarrow CH_{3(ads)} + H_{(ads)}$

Activation barrier of $CH_4 \rightarrow CH_3+H$

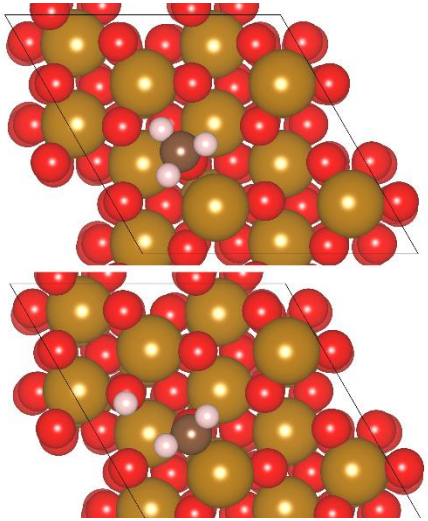
- We are currently working on the determination of the kinetics for initial C-H bond activation
- Nudged Elastic Band method with 6 images used to determine rough geometry, then refined with the dimer method
- Transition state structure is strongly distorted CH_4 tetrahedron, with C-H bond length 1.48Å
- Activation energy is 102 kJ/mol
  - This is quite high, unlikely to occur at room temperature, hence need for high temperature CLR





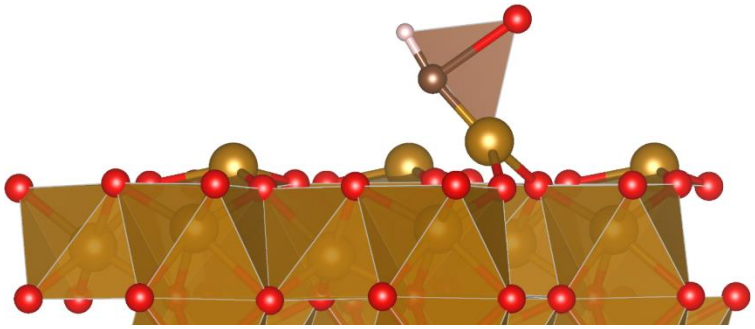
Thermodynamics of other structures

- Calculations on other reactions are ongoing
  - Particular area of concern is that the flat potential energy surface prohibits easy determination of the ground state structure
  - Hard to find vibrationally stable structures



- Approximate thermodynamics for other C-H bond activation events are:
  - 65 kJ/mol ($CH_3 \rightarrow CH_2+H$)
  - 493 kJ/mol ($CH_2 \rightarrow CH+H$)
  - 825 kJ/mol ($CH \rightarrow C+H$)

- Latter two steps are *highly endothermic*
  - This reflects extraction of lattice oxygen
  - Alternative process involving formation of formaldehyde/formate needs to be investigated



Future

- Complete reaction mechanism from DFT
- Kinetic Monte Carlo model for overall reaction
- Derived reaction rate constants for consumption of CH_4 and formation of final products (CO, CO_2, H_2, H_2O)
- First version REMARC scripts released and documented (June 2015)

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