Kinetic Monte Carlo Simulation of HCl Oxidation over RuO$_2$

Sergey Pogodin (spogodin@iciq.es), and Núria López (nlopez@iciq.es), Institute of Chemical Research of Catalonia

Motivation Behind the Project

Many processes in the chemical industry consume chlorine and reduce it to hydrogen chloride, highly corrosive and toxic substance, in amounts larger than it is demanded by the market[1]. Overproduction of HCl raises the question of its safe and cost-efficient disposal. Nowadays, electrolytic conversion of HCl to Cl$_2$ is widely used for HCl recycling, despite its high energy-consumption and the associated operational costs. An alternative way of Cl$_2$ recovery is the catalytic oxidation of HCl, possible at the surface of various catalysts, among others RuO$_2$-based ones performing most efficiently. Attractive due to the low energy demand, this relatively low-temperature process suffers from the problems caused by high price of Ruthenium and limited life-time of the catalyst under the reaction conditions. Thus, although successfully applied today in industry by Sumitomo Corporation, this process has not gained such widespread, as the electrolysis approach. It motivates further research[2-5] towards the better understanding of details of the RuO$_2$-catalysed HCl oxidation, and desirable enhancement of the process.

*Applications of the chlorine chemistry, shown[6] as the "Chlorine Tree".*
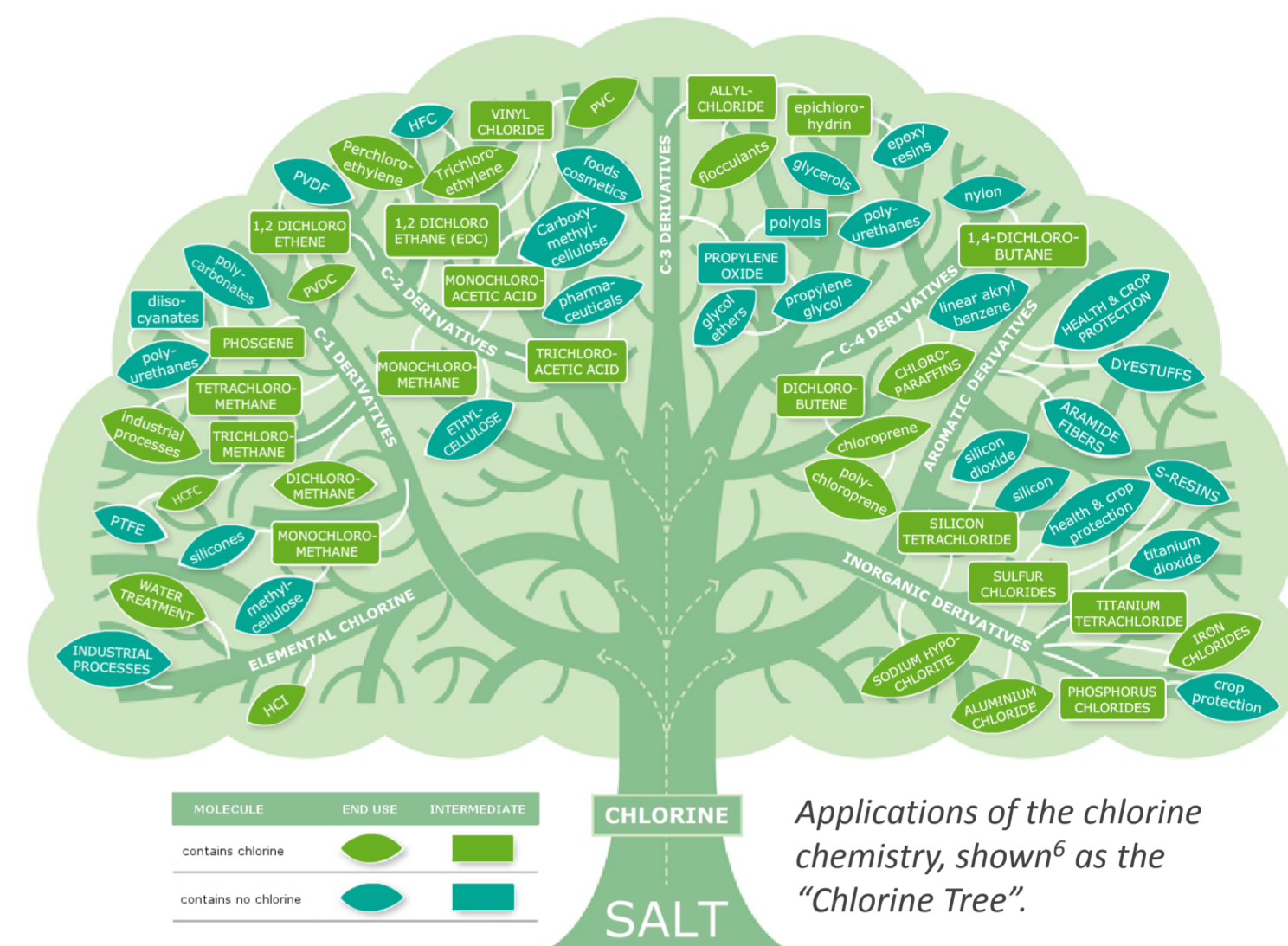
Our Mission:

To build accurate quantitative model of the catalytic HCl oxidation, applying Kinetic Monte Carlo approach to bring atomistic-level predictions of the Density Functional Theory to the process-relevant time and length scales. To acquire knowledge useful for further development of the catalytic HCl disposal.

Process Model

$$2HCl + \tfrac{1}{2} O_2 \rightleftarrows Cl_2 + H_2O$$
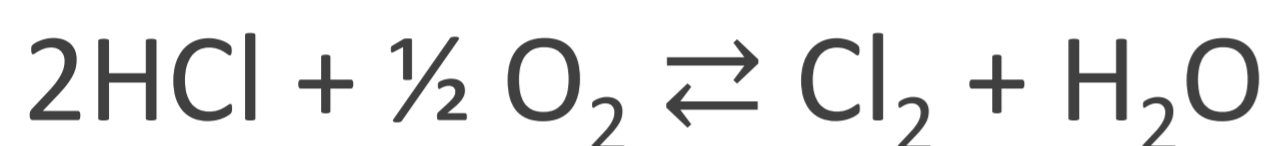
Catalyst's surface is simulated as regular lattice of cus (∗) and bridge (#) sites (corresponds to RuO$_2$ (110) surface, constituting 43% of catalyst nanoparticle's surface).
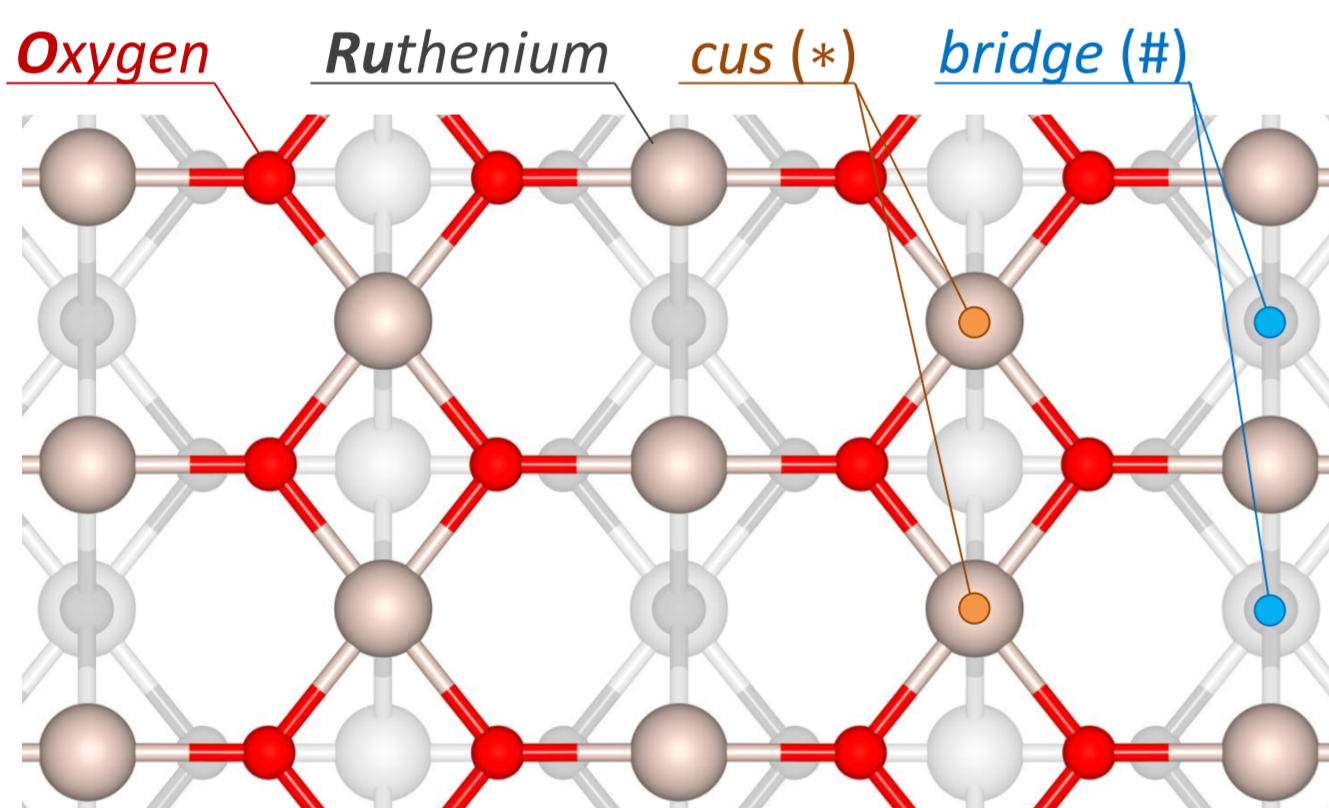
Structure of the catalyst's surface piece of size 5×2 sites (underlying layer is shown shaded).

Elementary reactions:

Adsorption, desorption, dissociation and association:

- HCl + O*$^{(\#)}$ ⇄ O*$^{(\#)}$HCl ⇄ OH*$^{(\#)}$ + Cl*
- HCl + OH*$^{(\#)}$ ⇄ OH*$^{(\#)}$HCl ⇄ H$_2$O*$^{(\#)}$ + Cl*
- O$_2$ ⇄ O$_2$*$^{(\#)}$ ⇄ O*$^{(\#)}$ + O*$^{(\#)}$
- Cl$_2$ ⇄ Cl*$^{(\#)}$ + Cl*$^{(\#)}$
- H$_2$O ⇄ H$_2$O*$^{(\#)}$

Surface diffusion:

- O*$^{(\#)}$ ⇄ O*$^{(\#)}$; Cl*$^{(\#)}$ ⇄ Cl*$^{(\#)}$; and OH*$^{(\#)}$ ⇄ OH*$^{(\#)}$

Hydrogen transfer:

- OH*$^{(\#)}$ + O*$^{(\#)}$ ⇄ O*$^{(\#)}$ + OH*$^{(\#)}$
- OH*$^{(\#)}$ + OH*$^{(\#)}$ ⇄ O*$^{(\#)}$ + H$_2$O*$^{(\#)}$
- H$_2$O*$^{(\#)}$ + OH*$^{(\#)}$ ⇄ OH*$^{(\#)}$ + H$_2$O*$^{(\#)}$

Energy barriers for the elementary reactions are determined from DFT calculations and later they are used to estimate reaction rates by analytical formulas from handbooks.

DFT Simulation

Density Functional Theory (DFT) calculations are used to determine the energies of the lattice pieces of size of 2×2 reaction sites, equivalent to the size p(2×1) (110), covered by reactive species in various patterns.

We use VASP with RPBE functional, PAW pseudo-potentials, 450 eV cutoff energy, 3-layered RuO$_2$ (110) surface slab, and CI-NEB to locate transition states.
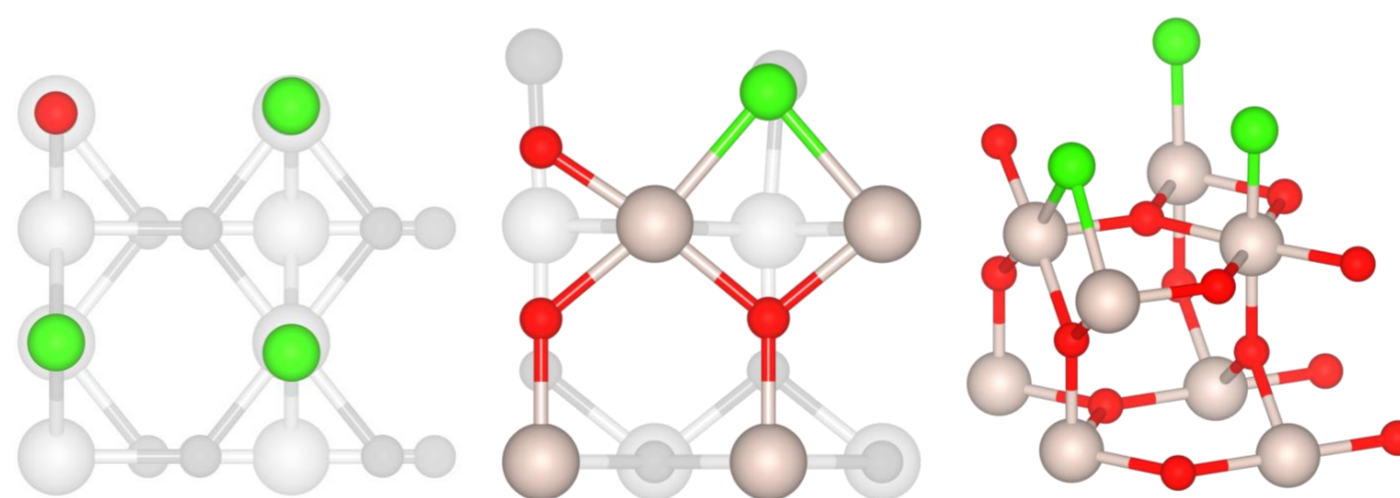
Snapshoot of the DFT simulation of the lattice piece of size of 2×2 reaction sites, with oxygen atom adsorbed to one of the bridge sites, and three chlorine atoms occupying other bridge and two cus sites. Left to right: top, left and 3D views.

Energies of arbitrary lattice pieces of sizes larger than 2×2 sites, covered by the reactive species in arbitrary manner, including the case with some atoms being in the transition states, are determined summing up the contributions of 2×2 subregions of the lattice piece.
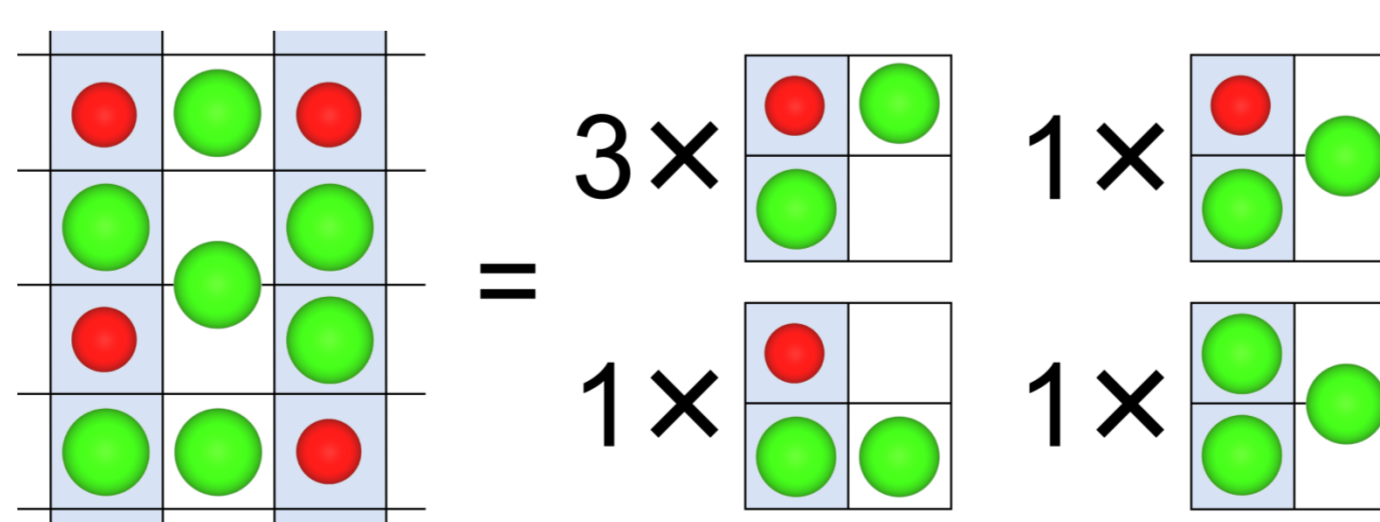

Schematic representation of decomposition of the energy of 3×4 lattice fragment, participating in Cl diffusion from cus to cus site, into contributions of six 2×2 regions of four distinct types. Blue shading denotes the bridge sites.

KMC Simulation

Kinetic Monte Carlo (KMC) simulation was implemented from scratch. Its current serial version features performance about 30 000 KMC steps per second, automatic estimation of unknown energies for 2×2 lattice regions (we limit the amount of necessary DFT calculations to those 2×2 regions which are encountered frequently during KMC simulation, or suspected to have significant impact on results due to different reasons).
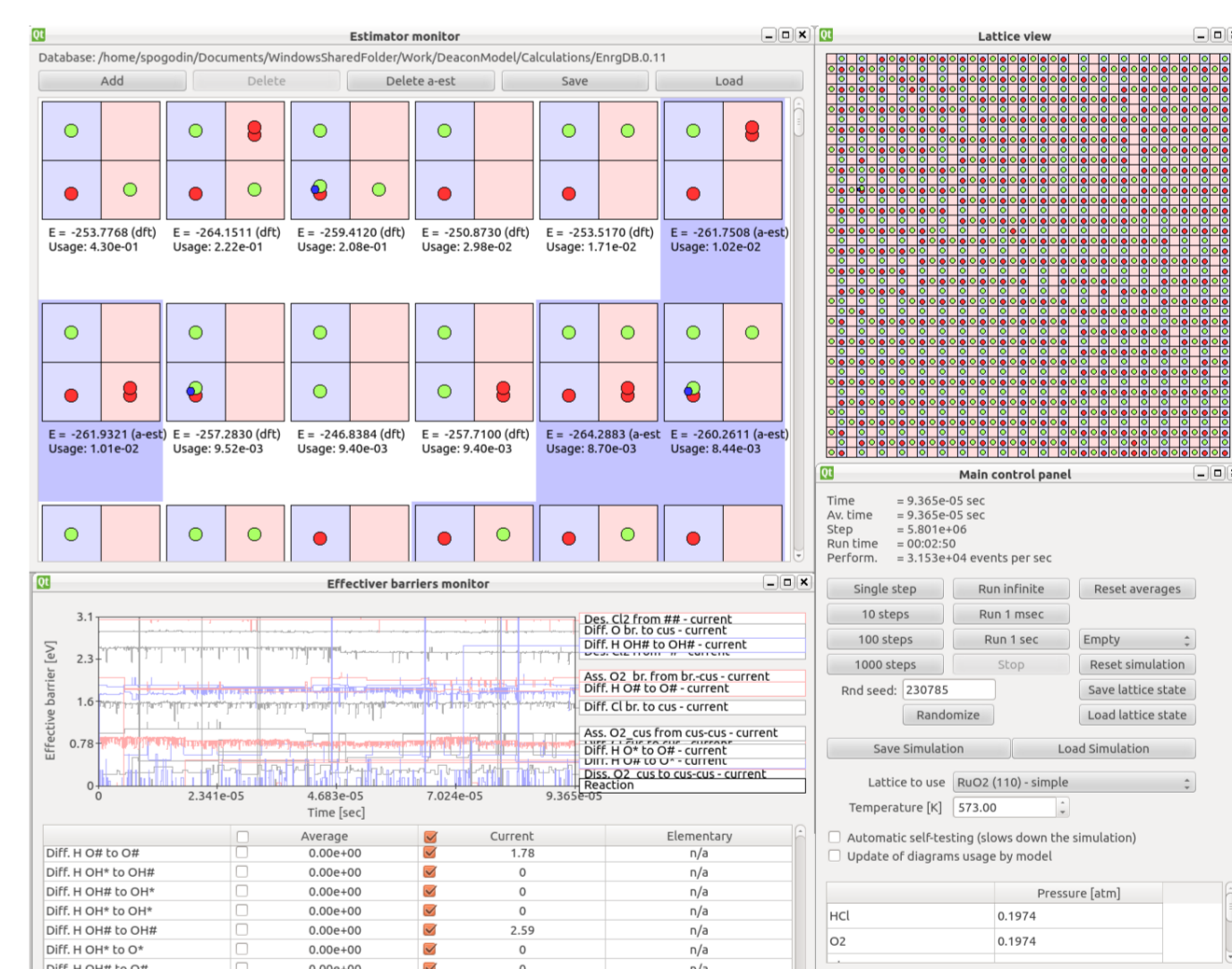
Snapshoot of the program GUI in course of the simulation.

- ●Cl$^\#$ ●OH$^\#$ ●O$^\#$ ●Cl* ●empty*
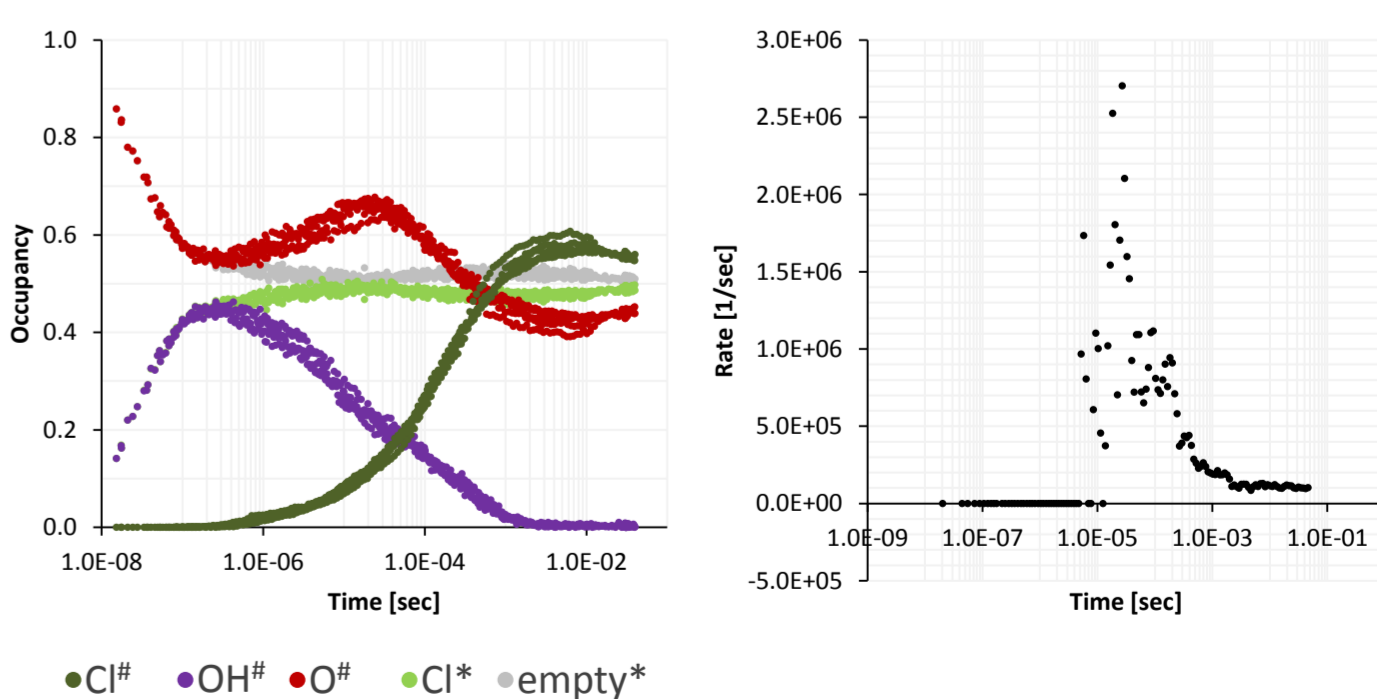
Lattice occupancy (left) and the rate of Cl$_2$ production (right) vs. time at fixed HCl, O$_2$, Cl$_2$ and H$_2$O pressures in the gas phase equal to 0.2, 0.2, 0.0, 0.0 bar. Initial configuration of the lattice is oxygen-occupied bridge sites and empty cus positions.

References

[1] Pérez-Ramírez, J.; Mondelli, C.; et al.; Energy Environ. Sci. 2011, 4, 4786.
[2] Teschner, D.; Farra, R.; et al.; J. Catal. 2012, 285, 273-284.
[3] Teschner, D.; Novell-Leruth, G.; et al.; Nat. Chem. 2012, 4, 739-745.
[4] López, N.; Gómez-Segura, J.; et al.; J. Catal. 2008, 255, 29-39.
[5] Over, H.; J. Phys. Chem. C 2012, 116, 6779-6792.
[6] Illustration from www.eurochlor.org

Created by Dr. Sergey Pogodin, April 2013