BIOVIA

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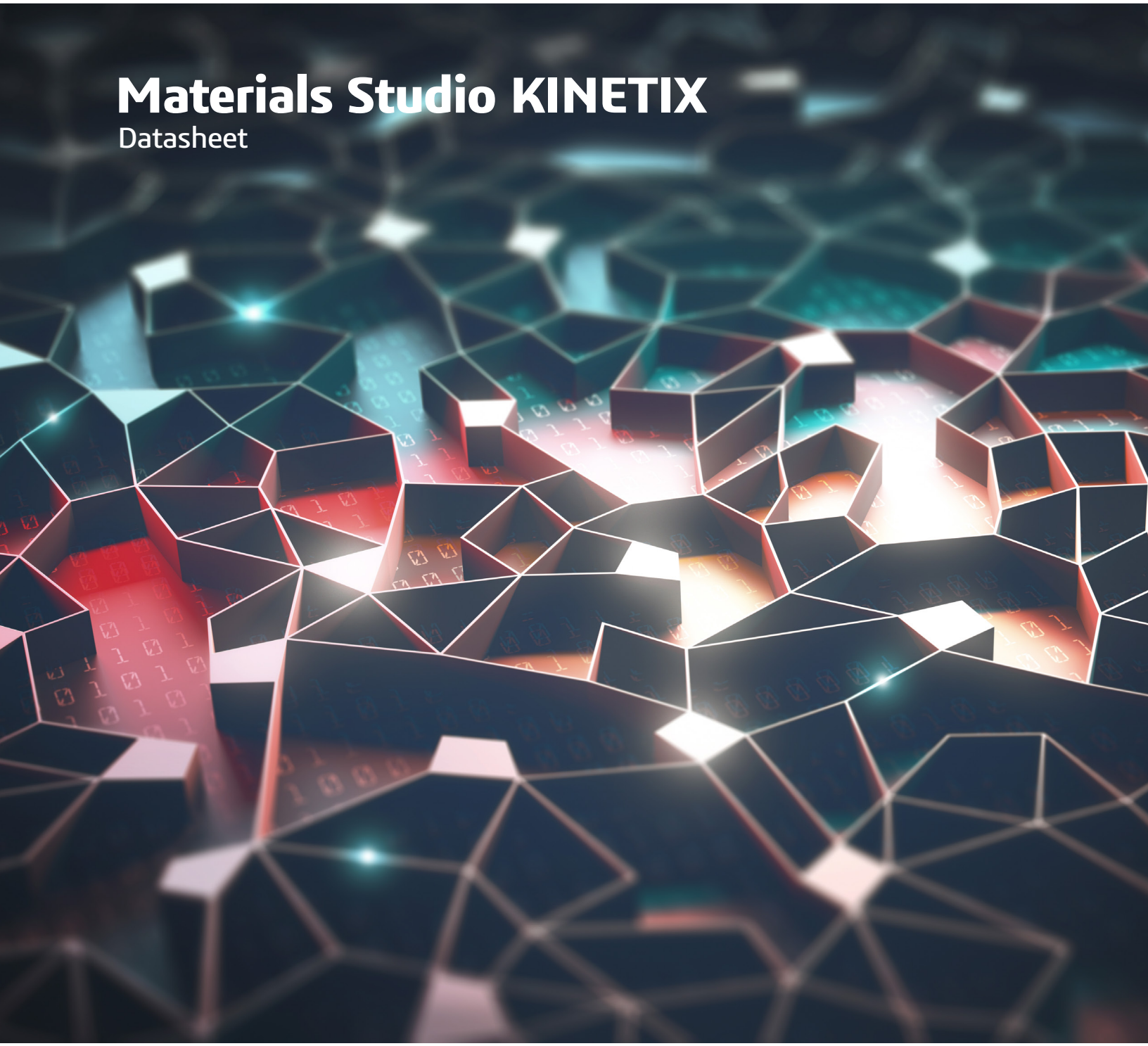
Materials Studio KINETIX

Datasheet



DASSAULT SYSTEMES

OVERVIEW

Accurately modeling reactions at catalyst surfaces requires a detailed knowledge of reaction kinetics in, what are more often than not, complex chemical mechanisms with multiple interdependent and competing reaction pathways. Reaction kinetics simulations provide predictions for the concentration of reactants and products, and their rates of formation, under a specific conditions and surface geometries. BIOVIA Materials Studio Kinetix uses a 2D-grid of reaction sites to represent the surface and uses the Kinetic Monte Carlo method to predict the surface occupancy. Consequently, Kinetix can provide the spacial distribution of the absorbed species as the reactions evolve with time to provide, amongst other things, unique insights into the role of surface diffusion processes in catalyst activity.

BIOVIA Materials Studio Kinetix supports these calculations by providing convenient way to define the input lattice geometry, manage the thermodynamic input and process data, launch the Kinetic Monte Carlo solvers, and manage, analyze and visualize the results within a single interface.

Amongst the thermodynamic information required to run Kinetix calculations, are reaction rate constants and pre-exponential factors that characterize the individual chemical reaction. For some reaction mechanisms these are readily available from existing reaction schemes, most often determined by laborious experimentation. For individual reactions that are not available, these inputs can be generated using quantum mechanical calculations to identify transition states between reactant and product states. Consequently, Kinetix can be considered a scale bridging technology linking chemistry at the atomistic level to macroscopic predictions of the performance of a chemical reactor (in this case a catalyst surface). It enables models to be developed using a bottom-up chemically detailed description of the catalyst surfaces and species which can be validated with experimental data. Tasks that contribute to that validation include temperature programmed desorption (TPD) procedure, which measures the temperature profile for desorption, indirectly quantifying the desorption energy. This is a preconfigured task where the outcomes can be directly compared with the equivalent TPD experiments.

In summary, BIOVIA Materials Studio Kinetix enables scientists and chemical engineers to make unique insights into predictions of chemical conversion at surfaces and to build validated models of the processes. These calculations provide characterization and optimization of catalyst performance, for exhaust-gas emissions, bulk and specialty chemical production, fuel cell development and fuel reforming, chemistry in battery cells, material deposition, plasma processing research and more.

WHAT IS KINETIX?

BIOVIA Materials Studio Kinetix is a general purpose program for the simulation of chemical and physical processes taking place at surfaces. Kinetix represents the surface using a 2D lattice of unit cells with periodic boundaries where each cell represents one or adsorption sites. The occupancy of these sites evolves using kinetic Monte Carlo methods, KMC through a number of stochastic moves; diffusion of the chemisorbed species, absorption and desorption transitions. The implementation of the KMC approach is based on the CARLOS simulation program developed at Eindhoven Technical University. The Kinetix module manages the configuration and generation of input files and jobs are executed from the BIOVIA Materials Studio Visualizer using the client–server gateway from a dedicated user interface.

KEY USES OF KINETIX

REACTOR DESIGN, OPTIMIZATION & IMPROVEMENT

Reaction kinetics simulations may be deployed in reactor design where the effects of modified reactor geometry and operating conditions can be explored in silico. By exploring the parameter space, process trade-offs can be quickly identified. The onset of reactions and controllability as a function of reactor conditions can be explored.

IDENTIFICATION & QUANTIFICATION OF EMISSIONS

Reaction kinetics simulations may be deployed to understand the byproducts of reactions, and in particular the sensitivity to process changes enables the chemical engineer to predict the downstream effects of process changes.

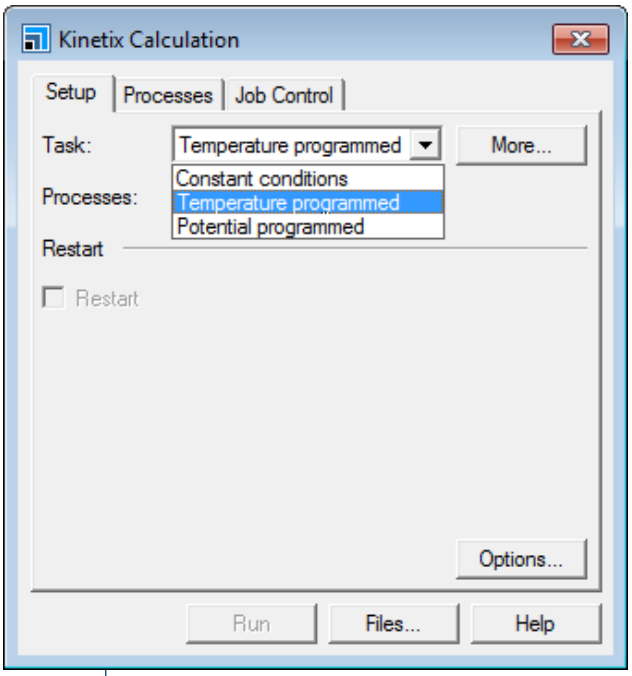


Figure 1. Kinetix Calculation dialog for task selection

HOW DOES KINETIX WORK?

The reactions at the crystal surface are specified as a collection of transitions, where a transition converts a pattern of the 2D lattice into a new pattern. Each such transition has an associated microscopic rate constant which determines the probability distribution of the time that elapses between the formation of the pattern and the occurrence of the transition. A simulation consists of a repetition of the following steps:

1. Identifying possible transitions.

2. Selection of a transition move and when it occurs.

3. Adjusting of the time and the lattice arrangement.

Most realistic simulations will contain multiple species, each with transition moves involving absorption, desorption, association, dissociation, reaction at a site or surface diffusion transitions between neighboring sites. Reactions are regarded as discrete events and the system is assumed to relax in between.

In this method, known as discrete event simulation, the state of the system evolves stochastically from probability distributions. There are two methods for implementing this available in Kinetix, the First Reaction Method (FRM) and the Variable Step Size Method (VSSM), where the efficiency of a specific method will depend on the processes involved, their reaction rates, and the current configuration.

BIOVIA Materials Studio Kinetix provides a convenient framework for managing the list of input parameters describing the various transitions and also the solver settings and execution of the calculations.

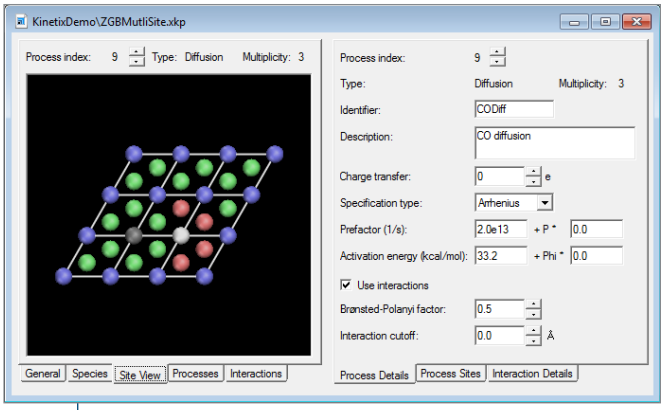


Figure 2. Image of a Kinetix Process document. Process documents contain information about the geometry of the lattice that represents a physical surface (cell parameters, cell symmetry, active sites), about species involved in the simulations, about elementary processes, and the parameters that define each process for a given system. The Site view allows individual processes to be defined. This example represents a diffusion process using a grid of top (blue) and hollow (green) sites where carbon monoxide diffuses to the grey (vacant) site from the white (occupied) site. This can only occur when the sites surrounding the vacancy are also vacant. The sites blocked by the presence of the adsorbed molecule are shown in red.

SETTING UP CALCULATIONS

The Kinetix tasks available through the Kinetix Calculation dialog allow specification of the parameters that determine simulation conditions such as temperature, heating rate, and simulation time. Details of a simulation are defined on the Processes tab of the Kinetix Calculation dialog and refer to the Configuration document and the Processes document specified on the Setup tab.

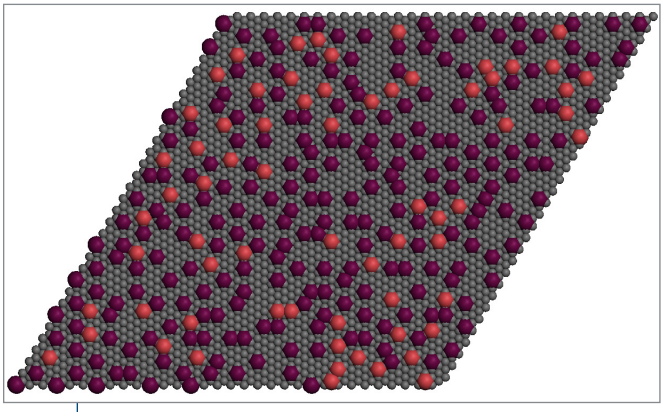


Figure 3. Surface configuration during a Kinetix simulation of CO oxidation on a platinum surface. Purple beads represent sites occupied by chemisorbed carbon monoxide and the red beads chemisorbed oxygen. Grey sites are unoccupied.

BIOVIA MATERIALS STUDIO KINETIX TASKS

CONSTANT CONDITIONS TASK

This task allows you to simulate time evolution of a specified system with constant external parameters, for example temperature. This task is useful for studying qualitative changes in the topology and pattern formation at different preset temperatures, is a way of equilibrating the initial structure, or as a way to investigate the relative roles of diffusion and reaction events before undertaking subsequent tasks.

TEMPERATURE PROGRAMMED TASK

This task allows you to simulate time evolution as the temperature changes, for studying the fundamental process of temperature programmed desorption, TPD. In this process the initial state is at low temperature with a certain adsorbate coverage of the surface. An equivalent experiment would be carried out in a vacuum chamber, with the rate of desorption recorded as a function of temperature. Correct description of experimental TPD results is a crucial test of the accuracy of a computational description of surface processes.

POTENTIAL PROGRAMMED TASK

This task allows you to simulate time evolution as the electric potential changes which is useful for studying a process such as voltammetry. In this the calculation simulates one electrode with a variable potential applied which affects the activation energies of each process involved.

KINETIX ANALYSIS DIALOG

The types of analysis that can be performed include:

- Display of plots showing the concentrations of various species over the course of the simulation

- Display of phase diagrams of species concentrations
- Display of plots showing the rates of processes over the course of the simulation
- Display of a voltammetry plot, showing the current flow across the surface over the course of the simulation

THE BIOVIA MATERIALS STUDIO ADVANTAGE

BIOVIA Materials Studio Kinetix is part of the comprehensive BIOVIA Materials Studio modeling and simulation suite. The integrated model building and editing tools enable you to construct, visualize, and manipulate molecular structures. Design based on experiment alone cannot address the complex requirements of large chemical kinetic mechanisms. Development of catalyst materials requires detailed understanding of the evolution of the reactions at surfaces. BIOVIA Materials Studio offers a single environment for the calculation of rate coefficients and their deployment in macroscopic chemical reaction simulation by combining experimental data with accurate ab initio predicted chemistry.

KEY FEATURES

- Model chemical reactions at catalyst surfaces
- Predict spacial distribution of absorbed reactants and products on surface
- Understand the role of diffusion in catalyst activity
- Connect ab initio calculations and reaction kinetics simulations within the same Materials Studio project
- Kinetix Configuration Builder
  - To create simulation lattices
- Kinetix Process Editor
  - for specifying species
  - for defining transition processes
- Kinetix Calculation tasks evaluate time evolution of system under
  - Constant Conditions – to find an equilibrium state
  - Temperature Programmed - as temperature changes
  - Potential Programmed – with a defined electrode potential field
- Kinetix Analysis
  - Concentration –plot concentration of species as a function of time or temperature.
  - Reaction rates– plot macroscopic reaction rates of species as a function of time or temperature.
  - Phase diagrams - plot the dependence of the concentration of one species on the concentration of another
  - Voltammetry - plot the current flowing across the surface as a function of time or potential

RUNNING JOBS

- All BIOVIA Materials Studio Kinetix jobs are run in the background freeing up the BIOVIA Materials Studio client for other research.
- All BIOVIA Materials Studio Kinetix jobs can be submitted to remote high performance compute servers.

To learn more about BIOVIA Materials Studio, go to 3dsbiovia.com/materials-studio

REFERENCES

R. Becker, Theorie der Wärme (Springer, Berlin, 1985).

A. P. J. Jansen, An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions (Springer, Berlin, 2012).

O. Kortlücke, V. N. Kuzovkov, and W. von Niessen, "Global Synchronization via Homogeneous Nucleation in Oscillating Surface Reactions", Phys. Rev. Lett., 83, 3089 (1999)

V. N. Kuzovkov, O. Kortlücke, and W. von Niessen, "Nucleation and Island Growth Kinetics on Reconstructing Surfaces", Phys. Rev.Lett., 83, 1636 (1999)

V. N. Kuzovkov, O. Kortlücke, and W. von Niessen, "Kinetic Model for Surface Reconstruction", Phys. Rev. E, 66, 011603 (2002).

D. A. McQuarrie, Statistical Mechanics (Harper, New York, 1976).

V. Privman, Nonequilibrium Statistical Mechanics in One Dimension (Cambridge University Press, Cambridge, 1997).

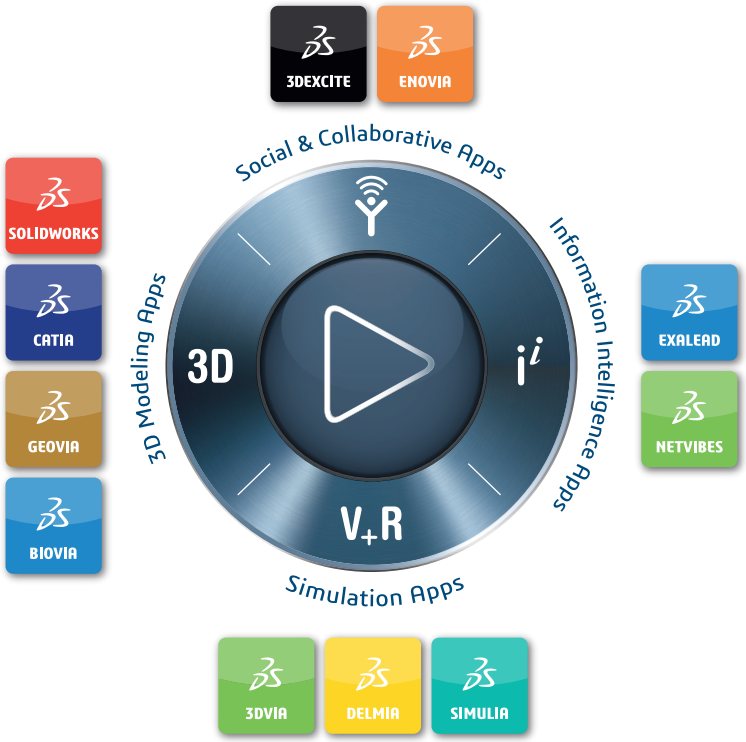
S. Redner, "Scaling Theories of Diffusion-Controlled and Ballistically Controlled Bimolecular Reactions", In V. Privman (ed.), Nonequilibrium Statistical Mechanics in One Dimension, 3-27 (Cambridge University Press, Cambridge, 1996).

R. A. van Santen and J. W. Niemantsverdriet, Chemical Kinetics and Catalysis (Plenum Press, New York, 1995)

G. A. Somorjai, Introduction to surface chemistry and catalysis (Wiley, Chichester, 1993).

J. M. Thomas and W. J. Thomas, Principles and Practice of Heterogeneous Catalysis (VCH, Weinheim, 1997).

R.M. Ziff, E. Gulari, Y. Barshad, "Kinetic Phase Transitions in an Irreversible Surface-Reaction Model", Phys.Rev.Lett., 56, 2553-2556 (1986)



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