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Automatic kinetic model generation for heterogeneous catalysis.

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Highlights
- Kinetic models for heterogeneous catalysis
- Use of cheminformatics for reaction and species 3D structure generation
- On-the-fly density functional theory calculations
- Benzene adsorption and oxidative coupling of methane as case studies

1. Introduction

Automatic kinetic model generation software has found its way in many academic and industrial research projects covering mainly combustion, oxidation, pyrolysis, and steam cracking, i.e. to build large gas-phase radical reaction mechanisms contain up to thousands of reactions. A translation of this software to other processes such as heterogeneously catalyzed reactions has been topic of a number of publications, often tailored to a specific set of applications. In this work, a novel approach has been developed to generate kinetic models over a broad range of applications, covering multiple active sites and surface orientations. Furthermore, the new tool allows to automatically start density functional theory (DFT) calculations for all the species and reactions in the kinetic model. The combination of automated generation of chemical mechanisms and DFT calculations enable computationally efficient screening of several catalysts for activity, selectivity and deactivation. The developed approach is illustrated by calculating adsorption energies for benzene on platinum surfaces and to generate a kinetic model for the oxidative coupling of methane.

2. Methods

A kinetic model generator typically consists of three general fundaments: molecular representation, reaction transformations, and termination criteria. These pieces are nowadays readily available in multiple software libraries, both in the public domain and in commercial packages. Open-source software is especially of great interest because of the generally fully disclosed source code, but also through the broad audience-based support and development, resulting in robust and flexible computer programs. For this work, the RDKit software [1] has been employed to take care of the molecular representations, reaction transforms and 3D structure generations.

To represent reactions of heterogeneously catalyzed reactive systems and surface species, we choose to define them by the adsorbent and a few "dummy" atoms to represent active sites. Several types of dummy atoms may be chosen to describe different adsorption sites, different surfaces or multifunctional catalysts. The reaction creation is done through a set of user-defined reaction families. These families may be defined in a very general way, e.g. desorption of an adsorbent, or for sub-categories of reaction families, e.g. the hydrogen abstraction from a primary carbon atom by a chemisorbed oxygen atom. Definition of reaction families allows to define rate rules, and to define constraints on which species are eligible to be a reactant in the given family. The latter may also be considered as a termination criterion for mechanism generation.

To screen several catalysts for descriptors for a chemical process, adsorption energies and rate coefficients are needed. Although many estimation methods exist for these parameters, they are limited to a particular application domain or a narrow range in process conditions. To broaden the range of applicability of reaction generation to heterogeneous catalysis, a computer code was developed to automatically perform DFT calculations using the *Vienna ab-initio Simulation Package* (VASP) [2], for which 3D coordinates of the adsorbate atoms are required. These are calculated using RDKit, including the dummy atoms.

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3. Results and discussion

Two case studies have been done: the adsorption of benzene on platinum and oxidative coupling of methane. To calculate the adsorption energies of benzene on platinum, the code first creates the 3D coordinates of benzene and the dummy atoms, shown in Figure 1a for the bridge and the hollow adsorption. Next, several surface orientations are created, and the dummy atoms are aligned with the coordinates of the surface atoms, c.f. Figure 1b. The *Atomic Simulation Environment (ASE)* [3] is used to handle the geometries of the surfaces and to place the adsorbates above the surface. 15 possible orientations of benzene exist on Pt(100), Pt(110) and Pt(111), 6 of them are illustrated in Figure 1c and have been successfully compared to literature data [4].
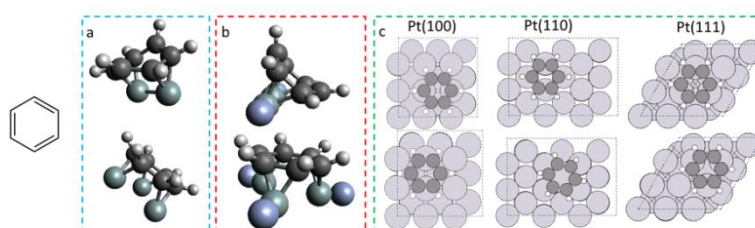

Figure 1. The generation of 3D coordinates for the benzene adsorption on platinum starting from the topology of benzene: (a) 3D coordinates of benzene and the dummy atoms for bridge and hollow adsorption, (b) 3D coordinates after alignment (blue atoms are active sites, green atoms are dummy atoms) and (c) final optimized benzene adsorption on Pt(100), Pt(110) and Pt(111). Only 6 of the final 15 orientations of benzene are shown here.

Oxidative coupling of methane is currently being studied as alternative source for fuels and chemicals from natural gas. Many catalysts have already been investigated experimentally or theoretically, and their findings have been reproduced in this work as a proof of concept of the methods. First, a literature kinetic model [5] for the heterogeneous catalyzed reactions during oxidative coupling of methane has been reproduced through the automatic kinetic model generator. Second, three important catalyst descriptors have been calculated: the reaction enthalpy of methane to a methyl radical and an adsorbed hydrogen atom, the dissociative chemisorption of oxygen and the adsorption enthalpy of a methyl radical. These have been calculated on several surfaces of Mn_2O_3 and Na_2WO_4, as illustrated in Figure 2.
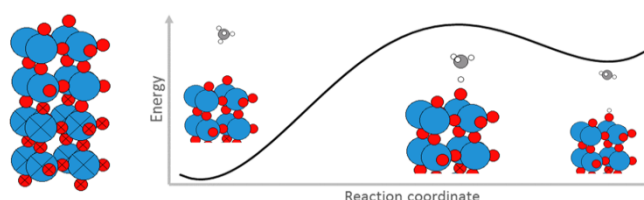

Figure 2. Activation of methane on a tungsten oxide catalyst.

4. Conclusions

A new tool and work-process has been developed to automatically generate detailed chemical mechanisms for heterogeneously catalyzed reactions through integration of open-source cheminformatics libraries and molecular modelling. The tool also allows the generation of 3D structures of catalyst surfaces and adsorbents to screen the surfaces for activity, identify most probable active surface orientations, selectivity on those and pathways of deactivation. This should enable a robust and fast assessment of catalyst performance and accelerate experimental research by theoretical guidance.

References

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