Interplay between carbon structures and their surface functionalization for improved hydrogen storage

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Motivation

Due to the ever increasing need of our society to get away from fossil fuel consumption, new ways to store energy in cost efficient ways have to be researched and improved upon. One possibility to store energy is in the form of hydrogen, which has a specific energy of 142 kJ/kg, the highest of any practical fuel. Since hydrogen has a very low density and a very low melting point, it is difficult or impractical to store significant amounts of it in a small volume.
Goal of my PhD is, with the help of atomic simulation, especially ab initio and molecular dynamics, to mimic the ability of carbon structures to store hydrogen and to point out possible approaches how this ability can be improved. On one hand the structure of the carbon networks regarding their capability to store hydrogen shall be analyzed and optimized, on the other hand particular attention will be put on the possibility of surface functionalization in regard to improved hydrogen storage capabilities. This surface functionalization is achieved by systematically adding lattice defects and doping atoms. Finally, this work is intended to contribute to the development of a hydrogen storage media with a sufficient high energy density, which can be used in mobile applications like hydrogen powered vehicles.

VASP

- VASP is the abbreviation for "The Vienna Ab initio Simulation Package".
- It is a package for performing ab initio quantum mechanical calculations using either Vanderbilt pseudopotentials, or the projector augmented wave method, and a plane wave basis set.
- The basic methodology is based on density functional theory (DFT).
- Basically by providing the code only the initial position of atoms, it can calculate the materials properties, like e.g. adsorption energies.
- VASP simulations are quite limited in the amount of atoms it can include (about 200).

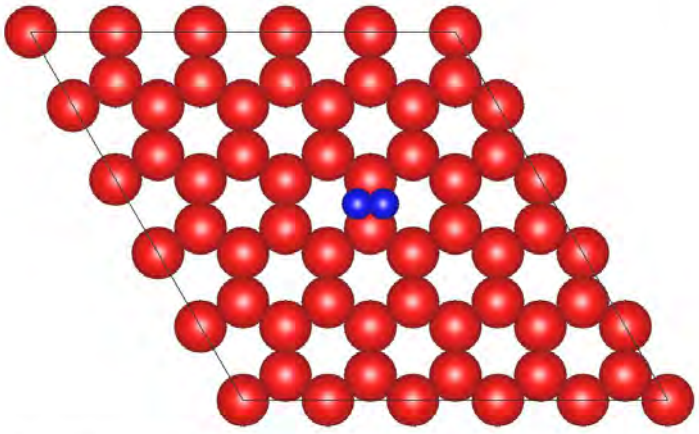

Fig. 1: VASP simulation of the adsorption of a hydrogen molecule (blue) on a graphene layer (red)

LAMMPS

- LAMMPS stands for "Large-scale Atomic/Molecular Massively Parallel Simulator" and is a classical molecular dynamics code with a focus on materials modeling.
- It is usually used for system sizes from a couple of hundred up to potentially millions of atoms.
- The simulations need a potential which describes all atomic interactions. While these are available for Carbon-Hydrogen systems, there are only a few containing additional elements.
- Nanoporous carbon structures can be created and their hydrogen adsorption capabilities simulated.

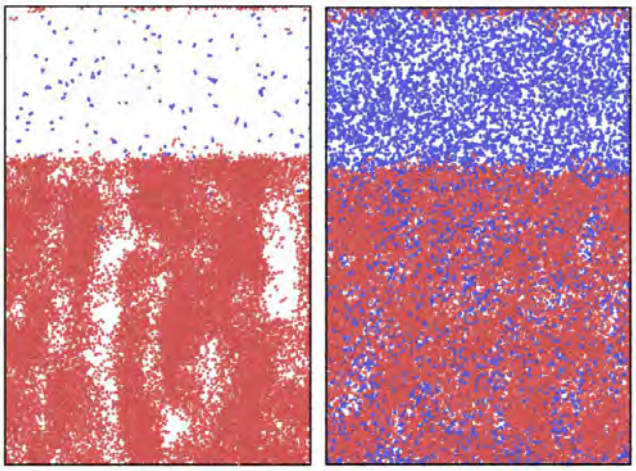

Fig. 2: Hydrogen adsorption in nanoporous carbon structures

Current state of the work

- Hydrogen adsorption energies for simple carbon structures like Graphene have been calculated by using VASP simulations
- Hydrogen adsorption kinetics have been observed using LAMMPS simulations.
- Bulk models from coconut shell derived activated carbon have been converted into an atomistic model.
- These models are used for simulations regarding hydrogen adsorption capability in dependence of temperature, hydrogen gas pressure and pore size.
- New methods to fit potentials for the use in LAMMPS simulations are investigated, like the ACE potential fitting.

Effects to take into account and how to simulate them

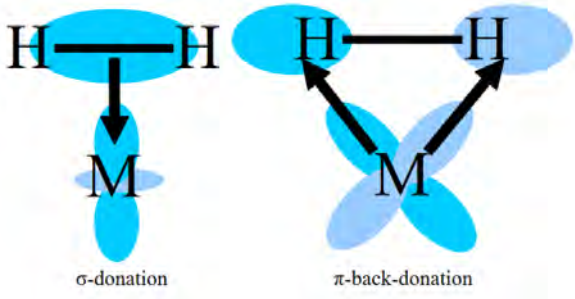

Fig. 3: Scematic of the hydrogen electron donation and TM-electron-backdonation of the Kubas effect

Skipper, Claire V. J. and Hamaed, Ahmad and Antonelli, David M. and Kaltsoyannis, Nikolas; The Kubas interaction in M(ii) (M = Ti, V, Cr) hydrazine-based hydrogen storage materials: a DFT study

- Pure carbon nanostructures will not yield a sufficient hydrogen storage capability.
- Only at liquid nitrogen temperatures and/or very high pressures nanoporous carbon is capable of storing relevant amounts of hydrogen.
- Two effects are important to take into account: The **Kubas Effect** and **Hydrogen Spillover**
- While the Kubas Effect binds the hydrogen molecule through electron exchange and a subsequent hydrogen bond length increase, Hydrogen Spillover completely breaks the H_2 bond and the H molecules get absorbed at the substrate surface.

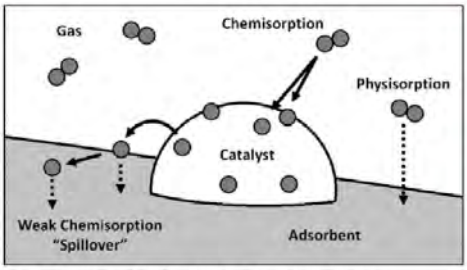

Fig. 4: Scematic of the hydrogen spillover mechanism

Hydrogen Spillover in Platinum-doped Superactivated Carbon 3.1 Overview. (2012).

- These effects have to be calculated in ab initio calculations and then fitted to an interatomic potential which can be used in molecular dynamic simulations.
- Potentials including carbon, hydrogen **and** a transition metal which might display these hydrogen adsorption phenomena, fitted for use in nanoporous carbon, is not available in literature.

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