Web Applications

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CatApp: A Web Application for Surface Chemistry and Heterogeneous Catalysis**

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Solid catalysts form the backbone of the chemical industry and the hydrocarbon-based energy sector. Most catalysts and processes today are highly optimized, but there is still considerable room for improvements in reactivity and selectivity in order to lower energy consumption and waste production. In addition, the development of sustainable energy solutions is a tremendous challenge to catalysis science and engineering. The ability to store solar energy as a fuel calls for new catalysts, as does the development of a sustainable chemical industry that is based on biomass and other non-fossil building blocks.

The development of new catalysts could be accelerated significantly if we had access to systematic data for the activation energies of elementary surface reactions. Once the key parameters that determine the activity or selectivity of a certain process have been established through experiments or calculations, such a database would enable searches for new catalyst leads. Ideally, data would come from detailed, systematic experiments, but it is generally not possible to find such data. Electronic structure calculations provide a powerful alternative. The accuracy is not such that detailed predictions of absolute rates of elementary reaction steps can be made, but for classes of interesting catalysts (such as transition metals) it is possible to create systematic data with sufficient accuracy to predict trends in reactivity.[1–16] Herein, we introduce such a set of calculated reaction energies and activation energies for a large number of elementary surface reactions on a series of metal single-crystal surfaces, including surfaces with defects such as steps. We also introduce a simple web application (CatApp) for accessing these data. The data will be part of a larger database of surface reaction data that are being developed under the Quantum Materials Informatics Project.[17]

The database includes reaction energies for all surface reactions that involve C–C, C–H, C–O, O–O, O–H, N–N, C–N, O–N, N–H splitting for molecules with up to three C, N, or O atoms on close-packed face-centered cubic fcc(111), hexagonal close-packed hcp(0001), and body-centered cubic bcc(110) surfaces, as well as stepped fcc and hcp surfaces. The metals included in the database are Ag, Au, Co, Cu, Fe, Ir, Mo, Ni, Pd, Pt, Re, Rh, Ru, Sc, V. The data have been compiled from previous reports,[18–23] where details of the calculations can be found. The key point is that the values have all been calculated with the same code (DACAPO), the same exchange-correlation energy functional (GGA-RPBE),[24] and similar calculational parameters. Therefore one adsorption energy or reaction barrier can be compared to another with some confidence. Gas-phase CO_2 and O_2, for which the RPBE functional performs poorly, were corrected as described in Refs. [25] and [26], respectively

In cases where there are no calculated data for a given reaction, we use the recently developed scaling relations to provide an estimate. The scaling relations link the adsorption energies of different molecules that contain varying amounts of hydrogen.[18] In a similar fashion, we exploit the fact that transition-state energies are quite generally found to scale with reaction energies.[1,22,27]

We have developed a simple visual query tool for accessing the data presented above. On our homepage,[28] we maintain a list of hyperlinks to the available versions of the tool, together with a list of references to the scientific data it employs. The tool is a web application implemented in JavaScript, SVG, and HTML, and runs in modern web browsers without any plug-ins. The application can be easily used on computers and portable devices with a touch interface. By running the application, one can choose a surface and an elementary reaction and be presented with a reaction path that reports the reaction and activation energy. If a DFT value is not found for a given reaction and a scaling estimate is used, the value is shown in italic type.

In Figure 1 we have shown an example of the use of the application. The energy barrier needed to break the N_2 bond on two different surface orientations of ruthenium, Ru(0001) and stepped Ru(0001), are extracted. The plots immediately show the structure dependence of this important step in the Haber–Bosch process ($N_2 + 3H_2 \rightarrow 2NH_3$). Our web application will allow anyone to download data such as that shown in Figure 1, and to quickly explore whether there may be other metals or structures where the N_2 bond is broken more readily.

All code and data are downloaded when the application is accessed for the first time and is kept in the local storage of the browser. This feature allows the application to be used even when the user has no internet connection. More importantly, it guarantees the user complete privacy, since all queries are performed locally in the browser and not by connecting to our server. The only information that is delivered from the user to our server is an anonymous

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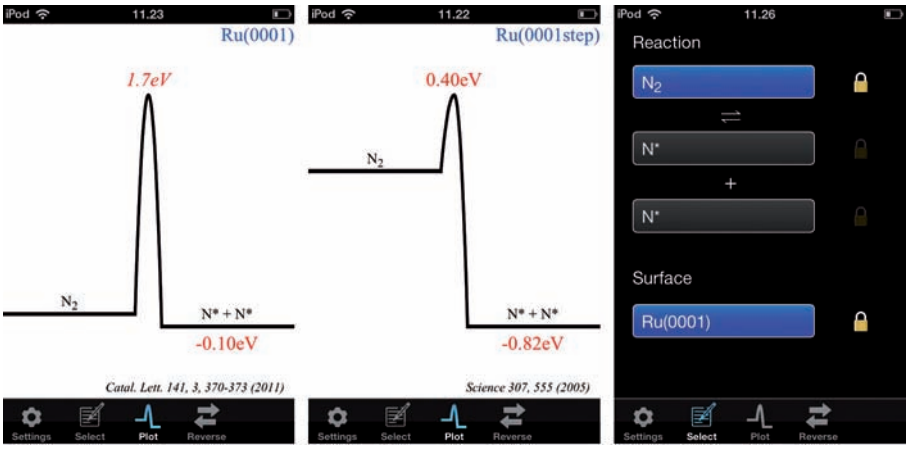

Figure 1. Screenshots from CatApp. Left and center panels: N_2 splitting on Ru(0001) and on stepped Ru(0001), respectively. Right panel: In the select view the user can from drop-down menus choose the reaction parameters (AB, A, B) and the surface parameter. When a parameter has been selected, the CatApp dynamically hides values of the unselected parameters for which neither DFT nor scaling energies are available.

transfer of the number of queries that have been executed since the last time the application was started while connected to the internet. These data will be used to monitor the use of the tool. On startup, the application will look for any updates to the application code or newly available data and seamlessly update itself.

The data shown in Figure 1 are direct copies of the output from the CatApp running on a portable device. The data are obtained by simply choosing the surface, the reactant, and the products from drop-down menus on the screen, as shown in Figure 1.

The database and web tool presented above is a simple forerunner of what will be available in the future. The database is a small subset of the calculated surface reactivity data that will be available under the Quantum Materials Informatics Project.[17] In the near future, the database will opened so that all researchers and research groups can submit their data to the database upon publication.

There is ample scope for making the database better and more useful by including coverage dependencies,[29] more surface structures including nanoparticles so small that they cannot be viewed as composed of independent facets,[30] and uncertainties in the calculations.[31] Alloy data will be uploaded next, and, as more accurate exchange-correlation functionals become available, such data will be made available as well. This will include data for reactions on oxide, carbide, nitride, and sulfide surfaces.

CatApp can provide the most basic tool for looking up reaction energies and activation energies. Again, there is ample room for introducing other tools, such as search tools, tools to correlate data (including the option of correlating measured data with the database), and tools to display calculated spectroscopic data for direct comparison to experiments. Another potentially useful option is to couple the query tool to standard databases of experimental data for gas-phase molecules and bulk solids, such as the NIST chemistry webbook,[32] and, eventually, to experimental data for surface reactions.

All the information in the database will be published data. The data will be tagged by a reference and the authors informed. A query tool such as CatApp will have the option of displaying all data or data from selected authors or papers. Therefore users of the data must refer to the respective papers if they want to include them in a publication of their own.

There is at least one other database of calculated properties of solids in existence focused at the moment on bulk materials for battery electrodes.[33] It will be highly desirable to be able to couple these and other databases together, but at the present stage the main challenge is to start a surface reactivity database and encourage the community to provide data and use them. Easy access to data by all researchers, both theorists and experimentalists, and academia and industry, is essential, and it is in that spirit that we introduce this surface reactivity and catalysis tool.

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