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Author(s)	De Chavez, Danjo P.
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Theoretical Study on Mechanically Stressed Chemical Systems (機械的応力下における化学反応系に関する理論的研究)

Mechanochemistry is the branch of chemistry that deals with the interaction of mechanical forces with any chemical system. In recent years, a surging interest was found in this field as evidenced by the amount of related research. This current revolution in the use of mechanical forces during reactions allowed the discovery of new chemical reaction and pathways, as well as molecular property tuning. Mechanical activation have been utilized in the fields of pharmaceutical chemistry, polymer chemistry, photochemistry, organic chemistry, among others. This growing application of mechanochemistry to various fields of chemistry has been rapidly increasing. However, elucidation of the reaction mechanism in situ remains very limited. In this regard, this current research aimed to build a fundamental understanding of mechanochemical reaction through chemical simulations and modelling.

The application of mechanical forces to a chemical system can be seen as an activation method which is an important aspect of catalysis. In comparison to the traditional modalities such as thermochemistry and photochemistry, mechanochemistry activates chemical reactions in a distinct manner. Mechanochemistry perturbs the potentials energy surface with a force vector. This force vector changes the energy landscape not only by its magnitude but also the direction in which it was applied. Application of forces to the chemical systems increases the dimensionality of the related potential energy surface. This renders the mechanochemical reactions exponentially more complex than the corresponding relaxed chemical reaction systems.

The chapter 1 of this dissertation is dedicated to the conceptual background where scientific origins of mechanochemistry was given in detail. Fundamental concepts in catalysis were also delineated and more importantly, the interaction of force and chemical reaction was discussed in the context of a theoretical diatomic molecule undergoing dissociation. It is common to assume a linear relation to activation and force. However, this often fails to capture the chemistry behind such assumption. Therefore, the limitations, pitfalls and failures of such linear assumption is also reviewed. As the last part of this chapter, the research scope of the dissertation is given.

Chapter 2 provides the reader a working knowledge of the density functional theory (DFT) which is used throughout the study. The discussion is initiated with a comparison of the wave function theory and DFT. This is followed by the historical development of modern DFT with the discourse and proof of the Hohenberg-Kohn theorems and the Kohn-Sham DFT is also discussed. The second part of this chapter is dedicated to the review of SIESTA and GPAW, linear scaling quantum chemical packages which are used in this study.

Chapter 3 of this dissertation is dedicated to the development of mechanochemical simulation tools and analysis. This covers a python module dedicated to mechanochemistry which can be used in tandem with several quantum chemical software packages. The usage of this Atomic Simulation Environment (ASE) extension is discussed with a tutorial.

A collection of theoretical studies of mechanochemical catalysis is given in chapters 4, 5 and 6. This included the effect of mechanical forces such as push and pull to the reaction center. In addition to this, the effect of strain in the catalyst to its catalytic activity is also studied.

In chapter 4, the mechanochemically induced selectivity in acid catalyzed hydrolysis in chitin sytem was investigated using mechanical pulling developed in the previous chapter. Pulling simulations were done using the Force Modified Potential Energy Surface (FMPES) formalism. Results show that deacetylation and depolymerization can occur simultaneously at relaxed systems. Upon the application of force, calculated activation energy for deacetylation remained unchanged. Depolymerization showed a decrease in activation energy. This change can be associated with a decrease in glycosidic dihedral angle with which electron donation to the glycosidic antibonding orbital is stimulated.

Following pulling simulations, pushing regime is studied in the context of mixed catalysis in Chapter 5. The stereoselective cycloprpanation in Ag(111) surface was done to probe the effect of spatial constraints in the reaction path and product selectivity. In this study, an unconventional slab sandwich model was employed to mimic the unique reaction environment of ball milling. It was found that the constricted reaction environment drives the reaction to the E isomer as seen in the experiment. In addition to this, activation energy was found to scale with slab distance separation.

In chapter 6, effect of mechanically strained catalytic surface is investigated. In this chapter, carbon monoxide dissociation in relaxed and isotropically, and anisotropically strained ruthenium surfaces is studied. Specifically, terrace Ru(0001) and stepped Ru(1015) surfaces was studied. Adsorption energies were examined not only in the context of the conventional d-band model but also the novel eigenstress model. NEB calculations were done and found that some pathways differed upon the application of strain. This exemplifies that mechanochemistry can change conventional pathways during chemical reaction. In addition to this, a break in the scaling relation was found. This originated with a difference in the slab interaction for the reactant and transition state.

Lastly, in chapter 7, a brief summary is provided. An outlook on mechanochemical research is also given as guide to future studies. Fundamental points of considerations in understanding mechanochemistry can be drawn from the several topics presented. The presented work can also serve as general simulation protocols to mimic the effect of forces in a variety of mechanochemical reaction system.