

Density Functional Theory (DFT) Calculations and Catalysis

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Catalysis plays a fundamental role in the establishment of sustainable chemical technologies that are efficient in terms of energy and atoms. Today, society relies heavily on petroleum oils, gas, and coals, which are utilized to produce almost all consumer goods, from fuels and fertilizers to polymers and pharmaceuticals [1,2]. Dependence on these nonrenewable raw materials increases the danger of global political and economic instability and is associated with the emissions of large amounts of greenhouse gases, generating widespread concern about climate change. This situation clearly creates an unsustainable future. New technologies must be conceived and realized in the near future to allow the direct use of alternative renewable raw materials and to make existing technologies more efficient and greener. Efforts towards the viable use of chemical feedstocks must be accompanied by efforts to make catalyst use more sustainable as well. This involves transitioning to more durable and active catalyst systems, preferably made from elements abundant in the earth. Consequently, the research of novel catalytic systems based on single atomic catalysts or nonprecious transition metals is a very active and dynamic area of research in the entire discipline of catalysis [3,4].

In the past two decades, computational chemistry has become one of the key components of catalysis research. Calculations have become very useful as they provide an interpretation of spectroscopic data and verification of catalytic mechanisms. Theoretical studies are suitable for studying chemical reactivity and modeling complex catalytic reaction pathways. Density functional theory (DFT) calculations have been a powerful research tool for decades [1–4]. Particularly, the knowledge and theory obtained from DFT-based calculations have effectively refined our understanding of fundamental chemical reactions, surface science, catalysis, and materials science [1,4,5]. In addition, it has been widely used for homogeneous reactions, heterogeneous catalysis, and electrochemical reactions. In this respect, the articles contributed in this book consider the fundamentals of DFT and related computational methods applied in homogeneous and heterogeneous catalysis, especially in the field of electrochemical catalysis.

Hao et al. examined hydrogen donation and transfer mechanisms of tetralin, by density functional theory (DFT) calculation, providing useful information on the role of H-donor solvent in direct coal liquefaction processes [6]. The authors showed that the order of hydrogen accepting capability from tetralin was α -H (C1-H) > δ -H (C4-H) > β -H (C2-H) > γ -H (C3-H). Moreover, they revealed that methyl derivatives more easily accept hydrogen from tetralin than benzyl derivatives. The overall results demonstrated that coal radicals can take hydrogen atoms from the H-donor solvent more easily than from hydrogen gas.

Xu et al. investigated the catalytic reaction mechanisms of the metal chlorides RuCl_3 , AuCl_3 , and BaCl_2 for 1,2-dichloroethane (DCE)-acetylene exchange reaction using density functional theory calculations [7]. The calculations revealed that acetylene-DCE complex is formed initially with low adsorption energy, and the following reaction to form vinyl chloride monomer (VCM) can be the rate-determining step. Indeed, they predicted the catalytic activity order of $\text{BaCl}_2 > \text{RuCl}_3 > \text{AuCl}_3$, which was experimentally verified. Overall, the different performances of the metal chlorides for the two different reactions for VCM production were successfully predicted and understood by identifying the reaction



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mechanisms, where the adsorption step was found to be important for the DCE–acetylene exchange reaction, while chloride transfer was crucial for the acetylene hydrochlorination reaction. The work thus provided useful guidance for designing catalysts for the DCE–acetylene exchange reaction, which can promote the development of highly efficient production of VCM.

Shen et al. studied the electro-reduction of the inverse metal oxide/metal catalyst using DFT calculations [8]. They used an inverse CeOx/Ag (111) model electrocatalyst as reducible oxides for CO₂ electrochemical reduction. The calculation revealed that Ag atoms acting as an electron donor are able to partially reduce Ce⁴⁺ to Ce³⁺ in the CeOx clusters forming the interfacial Ce³⁺ active sites, and this could facilitate the adsorption of and reduction in CO₂. Overall, it was suggested that the use of metal oxides to a metal electrode allows the interfacial active sites to adsorb and activate CO₂ and to promote further reduction processes. The metal species can provide good electrical conductivity, and the reductive metal oxides can guarantee an electron rich environment, which contributes to promoting the adsorption and activation of CO₂.

Fu et al. studied the effect of Co compounds (Co₃O₄, CoO and Co) on coal catalytic pyrolysis using benzoic acid (C₆H₅COOH) as a model compound of coal. They investigated the influence of the valence state change of the catalyst for coal pyrolysis process using DFT calculations [9]. The results showed that the energy barrier of C₆H₅COOH pyrolysis followed in the order: Ea(CoO) < Ea(Co₃O₄) < Ea(blank) < Ea(Co). Overall, the Co₃O₄ catalyst was confirmed to accelerate C₆H₅COOH pyrolysis via a partial reduction of Co₃O₄ to CoO, while Co showed no catalytic activity in C₆H₅COOH pyrolysis.

As an emerging application, graphitic carbon nitride (g-C₃N₄) has been introduced as an excellent catalyst carrier due to its large surface area, abundant reserves, stable thermochemical property, and facile capturing of single metal atoms. Zhou et al. studied the adsorption characteristics of C₂H₂ and HCl on single-atom catalysts of X/g-C₃N₄ (X = Au₁, Pd₁, and Ru₁), using DFT calculations to identify the catalytic reaction mechanisms of acetylene hydrochlorination [10]. The calculations revealed that C₂H₂ and HCl were well activated with the adsorption performance of C₂H₂ being better than that of HCl. They also found that the catalytic mechanisms of the three catalysts include one intermediate and two transition states. Moreover, the results showed that the three single-atom catalysts exhibited different activities with activation energy barriers increasing in the order of Au₁/g-C₃N₄ < Ru₁/g-C₃N₄ < Pd₁/g-C₃N₄. Moreover, the activation barrier in the Au₁/g-C₃N₄ catalyst was 13.6 kcal/mol, demonstrating the potential catalyst in the hydrochlorination of acetylene to vinyl chloride. Overall, this work gives useful insights to better design single-atomic catalysts for acetylene hydrochlorination.

Zhou et al. explored the photocatalytic activities and optoelectronic characteristics using doped bismuth oxyhalides (D-doped BiOX; D = Ag, Pd; X = F, Cl, Br, I) to investigate the atomic properties, optical properties, and electronic structures using DFT calculations [11]. The calculations showed that the photocatalytic performance of Ag-doped BiOX (X = Cl, Br) was much improved under visible light in comparison with Pd-doped BiOCl or BiOBr compounds. Furthermore, they found that Pd-doped BiOF showed a strong absorption under infrared and visible light spectrum, offering an effective direction to design a promising full spectrum catalyst. If Ag or Pd was doped in the BiOXs, all D-doped BiOXs exhibited a p-type semiconductor with all impurity levels from the D-4d state. Overall, these results demonstrated that the various optoelectronic properties and absorption coefficients of D-doped BiOX photocatalysts due to the electronegativity difference of halide and metal atoms would ultimately influence the photocatalytic performance of doped BiOX systems.

In summary, there is no doubt that excellent research is being conducted worldwide using DFT calculations for various types of catalysis, including conventional petroleum and coal upgrading, VOC decomposition, CO₂ conversion, and water splitting. This collection of publications features the progress and the latest trends in the constantly evolving field of DFT and catalysis. We sincerely thank the authors for their valuable contributions and hope that this Special Issue will inspire many researchers working in this field.

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