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Current opinion on the significance of promoting molecular modeling and simulation applications in Nigeria's future experimental catalysis and reaction engineering studies

T. Oyegoke[1,2]*, E. E. Peter[1], C. M. Igwebuike[3], B. El-Yakubu Jibril[1]

[1] *Ahmadu Bello University, Chemical Engineering Department, PTDF Catalysis Research Centre, Zaria, Nigeria*

[2] *Université de Lyon, ENS de Lyon, Laboratoire de Chimie, 69007 Lyon, France*

[3] *IMT Atlantique, GEPEA, UMR CNRS 6144, 4 rue Alfred Kastler, F-44000 Nantes, France*

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The practice of researching any subject in the field of chemical reaction engineering and catalysis among experimentalists *via* the use of a try-and-error approach in the search for an understanding of reaction kinetics and the development of a new catalyst for the optimization of production yield is already an outdated approach going by the recent advances recorded in the aspect of computational science. The practice is often characterized by a randomized process of searching for a solution with much unclear information and an unclear direction to concentrate on where a feasible solution can be obtained. Most studies that deployed this approach have claimed a massive cost of materials demand due to the unclear direction to focus the research effort. In this report, we present simplified highlights on the modern concept of deploying saving costs often incurred in laboratory studies *via* the presentation of the molecular modeling approach concept and its potential benefits in facilitating chemical reaction engineering and catalysis studies. The mini-review would aid in educating and captivating the interest of the developing nations' experimentalists toward appreciating the place of computational studies in easing and directing the focus of their research to aid in saving possible expenses that would have been incurred in the use of the old traditional approach which is often expensive. A hybrid approach deploying computational techniques like molecular modeling and simulation to give the experimental studies direction would go a long way in facilitating research among several groups.

Keywords: Molecular modeling, Simulation, Chemical reaction engineering, Catalysis

INTRODUCTION

There is a natural urge in man to comprehend the environment he lives in and, when practical, influence nature for the greater good of mankind. The prehistoric drawings seen in the 1940s by anthropologists when they first visited the Lascaux cave in France made complete sense to them. Their forefathers had made models of the animal motions they had to rely on for survival thousands of years ago. One of the primary forces behind scientific discoveries was the primal human need to comprehend, simulate, and imitate nature. Leonardo da Vinci designed the Vitruvian Man in the 15th century to depict the proportions of the human body. The drawing was carried out to better understand the nature of the workings of the physical body. Molecular modeling aims to achieve the same goal of understanding nature. Scientists produced the first molecular models after learning about chemical structure. The first molecular representations of methane, ethane, and methyl chloride were presented by August Wilhelm von Hofmann, a German organic chemist, in 1865 at the Royal Institution in London. He also established a system of colors for distinguishing elements still in use. In 1953, Francis Crick and James Watson presented the first 3D model of DNA, which is undoubtedly the most well-known instance of this type of modeling. The contemporary era of molecular modeling has been ushered in by building upon earlier findings in attempts to comprehend nature. Even in today's fight against COVID-19, molecular modeling is a viable tool [1].

Molecular modeling is a fast-emerging area used to model and simulate small chemical and biological systems to understand and predict their behavior at the molecular level. It has many applications in various engineering sciences, such as materials science, chemical engineering, biomedical engineering, and many other fields. Knowledge of computational chemistry is essential to understanding the behavior of nanosystems; it is probably the easiest route or gateway to the fast-growing discipline of nanoscience and nanotechnology, which covers many areas of research dealing with objects that are measured in nanometers and are expected to revolutionize the

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* To whom all correspondence should be sent:
E-mail: OyegokeToyese@gmail.com

industrial sector in the coming decades [2–4]. Since its advent, computational chemistry has grown to the state it is today and has become popular after immensely benefiting from the tremendous improvements in computer hardware and software during the last several decades. Computational chemistry can effectively solve complex chemical and biological problems with high computing power using parallel or grid computing facilities and faster and more efficient numerical algorithms [3]. This method can offer a wide range of benefits to various fields of study, like material analysis and design, reaction kinetics, catalysis, drug development, the design of corrosion-resistant materials, and many other applications. In any industry where the quality of products and improvements are centered on chemistry, the physical and electronic characteristics of materials can ideally benefit from molecular modeling [5]. The principle of molecular modeling has proven to be a valuable tool for providing predictive information ahead of any experimental studies. This can otherwise be seen as a pre-test to assess the innovative idea that a scientist or researcher experimentally synthesized in a wet laboratory. Such analysis can showcase the feasibility of such an idea and possible alternatives to achieve better the researchers' goal of synthesizing a defined material via a process and condition. In like manner, the molecular simulation tools can further find application in post-test studies where details would be explored at the molecular and atomistic scale level for the set of experimental observations made from the wet laboratory research studies.

Despite this wide range of advantages that the deployment of molecular modeling and simulation tools can potentially offer to experimental studies across different research subjects, a survey has shown that a lot of experimentalists are yet to embrace the deployment of these principles in their research works primarily in developing nations across different continents. Survey of experimental research works reported for developing countries in the literature indicates that the bulk of the reports does not deploy the use of computational approaches like molecular modeling in their studies; instead, they majorly focus on the use of only experimental methods. As the world continues to advance technologically, the need for these experimentalists (who are yet to understand the benefits this growing field can contribute to their experimental studies) to appreciate the position and significance of the computationalists (theoreticians) and not to take them for being game player who only engages in unrealizable activities is essential for experimental research advancement. There is also a need to appreciably promote the computational science field [6–8] and tools, seeing the level of contributions it has made in advancing and guiding experimental research works in advanced countries reported in the literature [7, 9]. One of the advantages it has provided is the potential to supplement the shortcomings of experimental sciences. These supplementary aids include providing pre-information (before beginning experimental investigations) on how to appropriately approach the specified research problems in a laboratory study. Another advantage of such an approach is its ability to provide post-information (after carrying out experimental studies) to reveal theoretical details (at the molecular scale level) on why a specific experimental study failed to yield the set of expected results or details theoretical explanation for any other experimental observations made in a practical and the way forward approach for addressing the issue or challenge. In addition, some of these details are sometimes difficult to obtain, access, or understand by experimental techniques and are typically given by computer simulations.

To address this poor level of awareness about the potentials that molecular modeling and simulation (an aspect of theoretical science) can offer to complement experimental sciences, especially in developing nations where only experimental studies are appreciated while disregarding the significant values of theoretical (or computational) studies, we presented in this report the various applications of molecular modeling principles which have successfully been used in advancing the research and development of chemical reaction engineering and catalysis studies in the most developed or advanced countries. Understanding the various benefits or applications of this principle *via* a mini-review of existing literature would go a long way to educating the developing communities to embrace it and promote strong collaborations between the experimentalists and theoreticians (or computationalists) in our communities for the advancement of science and technology in general.

Identification of reaction mechanism

Molecular modeling has enabled researchers to explore the intrinsic reaction mechanism of different catalytic or non-catalytic and homogeneous or heterogeneous reactions [10, 11]. The surfaces of materials are usually modeled in the form of either clusters or slabs shown in Figure 1.

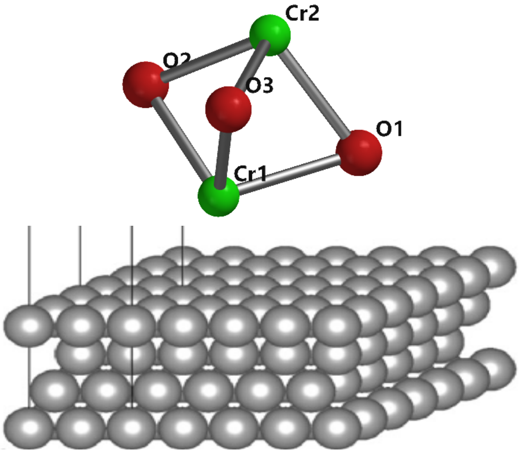

Figure 1. The Cr_2O_3 cluster model [12] and the Pt slab model [13].

The concept provides an understanding of the reaction path and the steps involved in the process. An example of a work that investigated the intrinsic reaction mechanism involved in the process is Oyegoke *et al.* [14], which studied the dehydrogenation of propane into propylene over the chromium oxide catalyst model, as shown in Figure 2. It highlights details on the effect of the participation of Cr-Cr and Cr-O sites in the oxidation of propane to yield olefin.

Understanding of reactions micro-kinetics

Chemical kinetics is a crucial study technique in the field of catalysis because the latter is fundamentally a kinetic process [16, 17]. Reactor design, reaction mechanism research, and explaining the structure-property link of a catalyst all require reaction kinetics data. Micro-kinetic modeling is utilized to better understand how to develop a catalyst to pinpoint crucial reaction intermediates and rate-determining elementary processes [18].

We now have a better understanding of the reaction involved in catalysis through the use of the micro-kinetics principle, which employs the results of molecular simulation and statistical thermodynamics calculation [19] to predict the evolution of both surface and gas-phase species throughout the reaction time for a certain amount of catalyst surface available at a specified time [19, 20]. The principles enable research to unveil the catalyst's performance in terms of yield, selectivity, and factor influencing the reaction’s kinetic and catalyst deactivation.

Facilitated material selection process in catalysis

It has further facilitated the drive toward selecting the best materials to improve catalyst performance. It has equally saved materials and financial resources employed in screening a wide range of materials in the development/re-designing of catalysts for a specific reaction in question [21].

Figure 3 gives a practical deployment of the adsorption profile in the metal screening to facilitate propylene desorption (where the more negative the value, the more difficult desorption would be from such a surface). The profile predicted that introducing Mo would best improve the ease of desorption of propylene from the catalyst [22] during the dehydrogenation of propane into propylene, a vital feedstock for petrochemical production.

Another case for applying molecular modeling in material selection is the computational screening of catalysts for the Haber-Bosch process for manufacturing ammonia [23, 24] which has confirmed the optimal catalyst of iron and ruthenium [25] within the dissociative descriptor of nitrogen graphically displayed in Figure 5.

Moreover, the major factor is that the structure and composition of the optimal catalyst are a function of the prevailing reaction condition. After the successful confirmation of the traditional catalyst for the Bosch-Haber process, the same group came up with a combination of less expensive materials of Mo-Co alloy [25], which give a better catalytic property for the ammonia synthesis (see Figure 6).

Understanding of reaction energy barrier or demand

Molecular modeling has enabled theoretical studies to provide insight into the overall or approximate energy demand (in terms of the barrier) that must be met for the yield to improve, which has to be engineered by design measures that reduce the reaction barrier. The barrier is often computed *via* either the apparent activation energy model [26, 27] or the use of the energetic span approach [28–31]. A scheme in Figure 7 shows the computation approach for estimating the overall reaction energy barrier using the energetic span approach. Three elementary steps were used to illustrate different possible catalytic reaction cycles that could be obtainable in a simulation study.

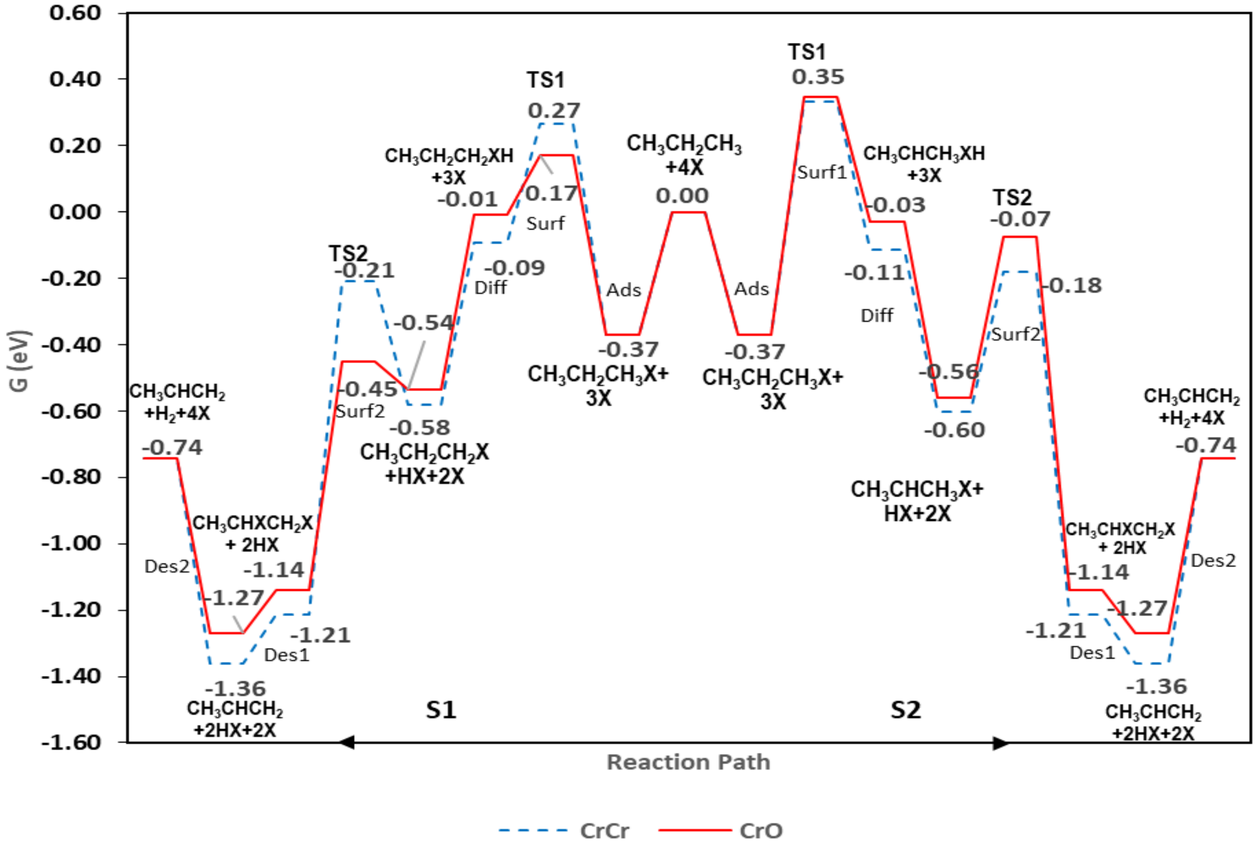

Figure 2. Propane dehydrogenation reaction mechanism profile over Cr_2O_3 [14].

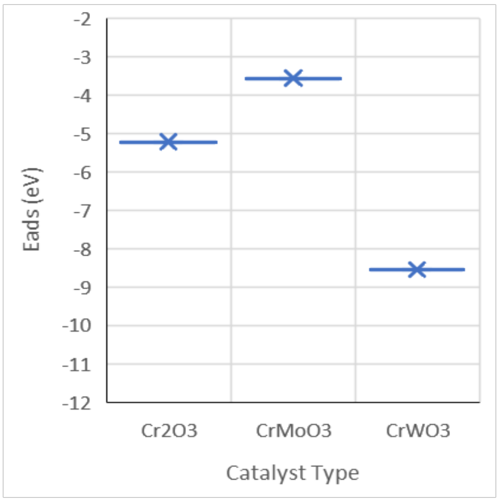

Figure 3. Adsorption profile for understanding the impact of Mo and Wo on Cr_2O_3 for ease of producing propylene [22].

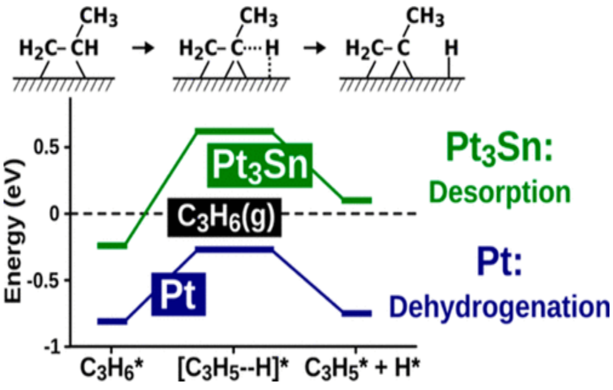

Figure 4. Plot showing the impact of alloying Pt with Sn in a propane dehydrogenation [15].

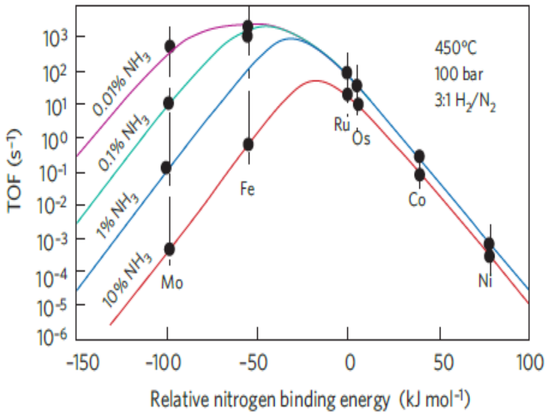

Figure 5. Volcano curves for the turnover frequency (TOF) calculated based on micro-kinetic modeling using parameters calculated by density functional theory (DFT) [25].

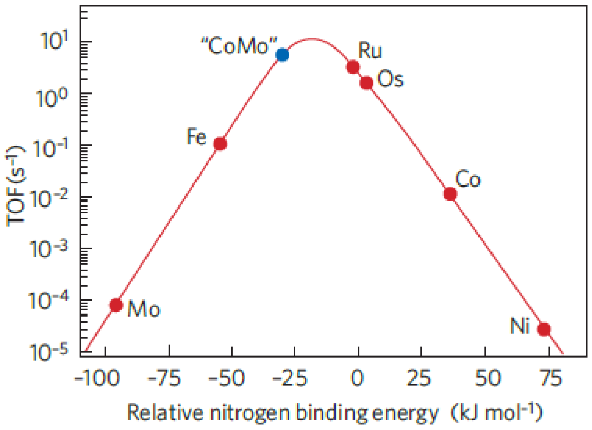

Figure 6. Interpolation concept illustrating that binding energy for a CoMo catalyst is intermediate between the elemental catalyst Co and Mo [25].

The first case in Figure 7a is the single cycle model, which shows two sub-cases in blue (less energetic, flat, and efficient reaction profile) and red (low energy profile). In the blue case, a less stable intermediate compared to the reaction starting state (Io), where the energetic span was computed as the difference between the higher transition state (TDTS, that is, TOF-determining transition state) with the initial reaction state (Io) which was taken as the most stable intermediate (TDI, that is, TOF-determining intermediate) since no intermediate is less stable than Io. Another case, tagged as the red case in Figure 7a, shows a model stable intermediate (I_2) than the initial state of the reaction (Io), which makes I_2 become the TDI in such a case [28–31]. The cases presented for the single-cycle model in Figure 7a are possible cycles often expected during the catalysis of a chemical process.

However, some unexpected activities like the formation of the off-cycle intermediate, which are reversible (that is, Cx to Cy in Figure 7b), or catalyst deactivation, which are irreversible (that is, Cx to Cd in Figure 7c), are sometimes confirmed for some catalytic processes studied. In a case where the off-cycle intermediate (I_y) occurs and appears more stable than the on-cycle (I_x) one, the off-cycle intermediate (I_y) would be taken as the TDI. Using the catalyst deactivation model [31], we can compute the catalyst's turnover number (TON) in a simulation study. The TON value accounts for the mean cycle numbers a catalyst molecule can provide before deactivating. It can also be referred to as a catalyst's life span or expectancy, after which the catalyst remains inactive.

Another approach for computing the overall energy barrier in a chemical process studied is the use of a micro-kinetic simulation approach, where the reactor model and some other conditions are taken into consideration in such an approach. Some codes like MKMCXX, Micki, and many other micro-kinetic simulation codes have been developed to facilitate the deployment of the technique in chemical reaction engineering and catalysis studies. Moreover, these approaches' applications have been reported in the literature. Some works include one that attempts to evaluate the impact of Sn on the Pt [15] when alloyed together (in Figure 4), where the barrier was used to understand its role in influencing the catalysis. Figure 2 shows the effect of having a higher concentration of chromium site (Cr-Cr) in the CrO-based catalyst surface and a case of when oxygen participated (Cr-O) in the catalysis to reduce the activities of the chromium site. With the use of molecular modeling using density functional theory (DFT) calculation, Peter *et al.* [32] predicted promoting ZSM-5 catalytic activity of propane dehydrogenation with the introduction of gallium over zinc metal. The authors reached such deductions using the activation barrier of the rate-determining step identified in the study.

Improved rate of catalyst development

Every approach towards establishing atom and energy-efficient sustainable chemical technology relies heavily on catalysis. The improvement in understanding catalytic processes' fundamentals has been extensively facilitated by computational modeling and molecular simulations.

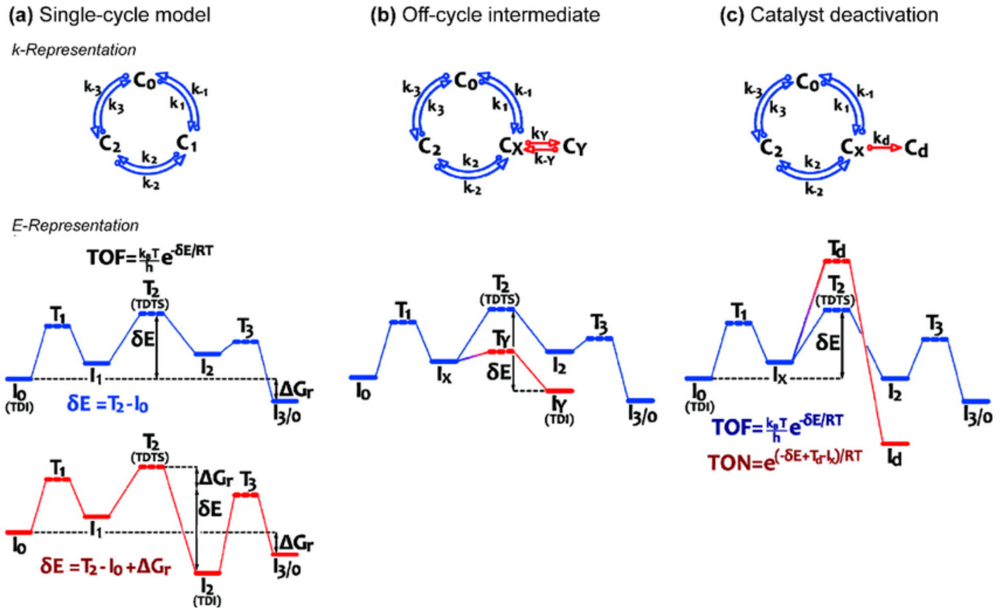

Figure 7. A pictorial illustration of the energetic span approach deployment in search for insight into the kinetics of a reaction mechanism where three cases are presented [31]: (a) single-cycle model, (b) off-cycle intermediate, and (c) catalyst deactivation.

The evaluation of spectroscopic data and the clarification of catalytic mechanisms depend very well on computations for an atomistic framework [33]. Concerns about the environment, resource use, safety, and overall process efficiency are some factors driving the continual search for the best process conditions and catalysts [7]. Previously, the majority of research in catalysis has been experimental. Although this is still the case, molecular modeling, and simulation are already widely acknowledged as crucial tools for the research and development of catalysts. Molecular modeling can offer fresh perspectives on reaction pathways, forecast the characteristics of catalysts yet to be developed, and integrate data for a given system from various experimental techniques into a single, logical image. Modeling and experimentation should work together, that is, in synergy; experiments should validate modeling while modeling should describe the results of an experimental study, indicate new ideas and scientific testing, or possibly replace laboratory tests in the screening of various process conditions or catalysts [34].

The use of computing facilities to theoretically carry out a pre-evaluation of the idea proposed on the right approach that best suits the modification/design of a catalyst for a specific reaction has dramatically promoted the speed at which the catalysts are developed across the globe, unlike the traditional approach of doing without it [20, 35].

Spectral findings by density functional theory

For a better understanding of the catalyst surface and intermediates proposed during the search for reaction mechanisms, which are the key ingredients for micro-kinetic modeling, the importance of spectroscopy must be emphasized. With the increased sophistication of the DFT and the incorporation of time-dependent DFT, the initial problem encountered with the Hartree Fork (lack of electronic correlation and calculation at ground state) in spectroscopy findings has improved significantly [36]. Theoretical spectroscopy such as ultraviolet–visible (UV-VIS), Raman, nuclear magnetic resonance (NMR), and infrared (IR) has thrown more light on experimental studies and given a better understanding of the nature of the surfaces and the intermediates involved during reaction [37–39]. Using advanced methods in molecular modeling and simulation tools, we can now effectively model and simulate different spectra for the vast range of materials synthesized in the wet laboratory. Some research in the literature [14] does deploy the use of these spectra to validate the material synthesized in the laboratory to understand better what kind of peaks are expected using the molecular modeled materials' spectra to identify if the type of material of interest is present in the product obtained using the set of peaks in the spectra. Like the case of synthesizing silicon oxide from rice husk materials [40, 41], pure silicon oxide spectra can be obtained *via* the deployment of molecular modeling tools and be used to compare with the spectra obtained for the synthesized products instead of the traditional approach of using the standard table presented in chemistry books or literature to confirm the functional groups of the set of peaks found in the Fourier transform infrared (FTIR) spectra and many other applications.

CONCLUSIONS

Molecular-scale simulation has reached a stage of sophistication and accuracy, making it an essential field for chemical engineers and other physical scientists. These extensive applications of molecular modeling principles to reaction engineering and catalysis primarily have a strong capacity to save material resources incurred in catalyst development and chemical production process optimization studies. The promotion of the hybrid mode of studying reaction kinetics and catalysis would unfold in more detail about the factors responsible for several experimental observations made in a wet laboratory study. It would aid in providing roadmaps or compasses in terms of having preliminary insight into a clear pathway or procedure that has better feasibility of solving the defined research problem, unlike the deployment of the usual try-and-error design of experiments. Therefore, harvesting the benefits of this hybrid mode of studying the chemical processes would require the experimentalists' mutual agreement and readiness to collaborate with computationalists, otherwise known as theoreticians, to complement each other in ongoing and future research.

Conflict of Interest: *The authors declare no conflict of interest.*

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