Miniature Physical Sphere-in-Contact Models of Heterogeneous Catalysts and Metal Nanoparticles

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Abstract

Context

Physical molecular models have played a fundametal role in the understanding of chemical reactions on heterogeneous catalysts and on metal nanoparticles. To date these physical models have been based on separate models of the metal nanoparticle (NP) or surface, of the substrate and the molecular structure of reactant and product adsorbates and their intermediates. In this paper we try to provide a new miniature physical molecular model, the sphere-in-contact model of heterogeneous catalysts and metal nanoparticles that can build inexpensive, small and efficient molecular models that can be transported or shipped easily and that depict the chemical reaction as a whole, showing reactants, intermediates, products, the metal nanoparticle bound to the substrate which can give information about a reaction mechanism. These models reveal that there are certain rules with respect to the kind of sites you observe at the metal NP interface with the support by small movement of the nanoparticle.

Methods

We have used in this study physical molecular models using the sphere-in-contact model. This is the first time such physical models are build for heterogeneous catalytic reactions and metal nanoparticles and they are constructed out of spheres that fuse together when exposed to water.

Keywords: Sphere-in-contact, molecular models, equal, heterogeneous, catalyst, metal nanoparticles, H

1. Introduction

The use of molecular models has played an important role in the development and the discovery of new facts about materials and biological molecules. Molecular models were used very early on in science with some molecular models of benzene having appeared in 1865 from the scientist Auguste Kekulé.[1,2] Watson and Crick used physical ball-and-stick models to elucidate the structure and base pairing of DNA.[3] Linus Pauling used ribbon models to find out how the hydrogen-bonds are aligned in the alpha-helix.[4] The Bragg's, father and son, used molecular models to present their discoveries from X-ray crystallography.[5] It is unquestionable that with the advent of computer simulations, the use of molecular models has been reduced, and it is more efficient to generate and manipulate molecular structures of catalysts via computer programs and through simulations. However, the use of physical molecular models in teaching is still very important nowadays as they offer a different mean of presenting molecular structures, one that can be manipulated and therefore offer in some cases more information to the learners/researchers. They are also useful for practical learners as opposed to visual learners. We have previously shown that there are four different physical molecular models (See Fig. 1) for carbon materials, the space-fill model[6,7], the ball-and-stick model[8,9], the wireframe model[10], and lastly the sphere-in-contact model[11] and that there are some advantages in the sphere-in-contact model especially when modeling the cap structure of carbon nanotubes.[12,13]

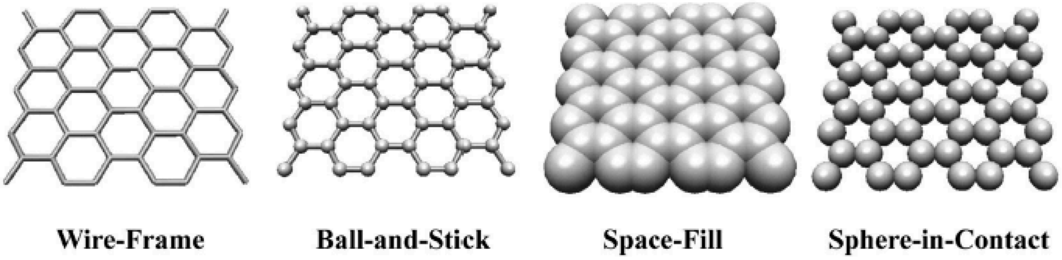

Fig. 1 The four physical molecular models, Wire-Frame, Ball-and-Stick, Space-Fill and the Sphere-in-Contact model for a graphene nanoribbon. Structures drawn with Nanotube Modeler[14] and reproduced with permission from Ref.[15].

Molecular modeling techniques have revolutionized the study of heterogeneous catalysts and metal nanoparticles, providing valuable insights into their structure, reactivity, and catalytic performance.[16] Heterogeneous catalysts play a critical role in numerous industrial processes, while metal nanoparticles exhibit unique properties that make them attractive for various applications, including catalysis, sensing, and biomedical technologies.[17] Molecular models enable researchers to understand and predict the behavior of these systems at the atomic and molecular level. Molecular modeling of heterogeneous catalysts involves the representation and simulation of the catalyst surface, the adsorption of reactant molecules, and the subsequent reaction steps. Although the modelling of heteregeneously catalysed reactions has relied on computational approaches[18] such as density functional theory (DFT)[19], kinetic Monte Carlo (kMC) techniques and molecular dynamics (MD)[20] and most of this research has relied on the use of personal computers and high-performance computing facilities, physical molecular models are still useful in teaching and in research in many labs around the world. We therefore wanted to provide a physical molecular model that can show the molecular system of a reaction occuring on a heterogeneous catalyst in detail, meaning that you can show the reactants and products in their chemisorbed/physisorbed state on the catalyst. Furthermore, it can show the structure of the catalyst as well as the bonds at the interface between metal NP and substrate. This means that the adsorption site geometry can be clearly seen as well as the structure at the nanoparticle-substrate interface. The sphere-in-contact models in this study have been built using plastic spheres that bind together when exposed to water. These materials are quite inexpensive and can be purchased from various companies on the internet.

The rest of this study has the following structure. We first give a historic overview of the use of spheres in physical molecular models. We then describe the sphere-in-contact models of various metal nanoparticles followed by the sphere-in-contact models of various adsorbates adsorbed on cubic and hexagonal NPs. We then present the models of ammonia synthesis and the water-gas shift reaction on various metal supported catalysts and we finish with the structure of various molecules using the sphere-in-contact model.

2. Methods and Metrials

The sphere-in-contact models were constructed with plastic spheres that were pilled with a tweezer. The spheres fuse together when exposed to a small layer of water. These spheres were 5mm in diameter and therefore will construct models of carbon materials (i.e. graphene, graphite, fullerene, carbon nanotubes) that have a scale of 1: 0.28×10^{-7}. This water can be dispensed via a spray or dropper and the excess water has to be removed by holding the template tray 45° with respect to the surface of a dry napkin, so that the excess water drips away. It is less time consuming if the beads in making the nanoparticle are removed from the template tray, before they complete dry, using a spatula (see Fig. 2) and be dried with hair dryer using cool air. The metal nanoparticles are constructed by pilling the spheres on the hexagonal or square template in several layers, each higher layer having a smaller total area than the layer beneath. One can construct spherical NPs by making two halfs of a NP and glueing them togther with Bison super-glue. The reactant and product atoms are bound together with Bison non-drip super-glue 1g which is applied on one surface of the sphere and the second surface is brought into contact with the first for 10 sec, which generates a firm bond between the two atoms. The models of the substrate and metal NP are separately build and glued togther with super-glue.

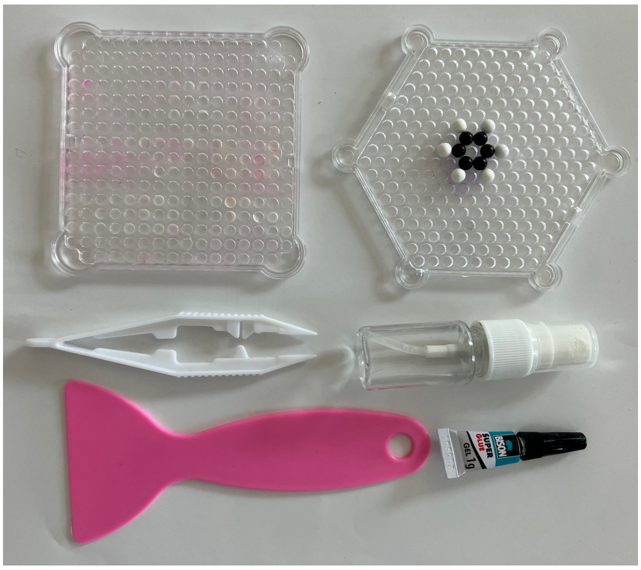

Fig. 2 Materials and tools used to construct sphere-in-contact models of chemical reactions happening on metal supported catalysts.

3. Results and Discussion

3.1 Stucture of metal and support nanoparticles

The sphere-in-contact model can form realistic physical models of metal nanoparticles having different facets on their surface and progressively larger number of atoms in the metal nanoparticle (NP). Currently there are commercially two-grids available for placing the spheres in a regular arrangements.[21] There is a square pattern and there is also a hexagonal pattern. The base of the NP in the hexagonal pattern can either be triangular or hexagonal, as depicted in Fig. 3(a). The NPs with the trigonal base form facets that are (111)-like whereas the NPs with the hexagonal base form both (100)-like and (111)-like facets. Both these structures are known from the 15th centuary when Thomas Harriot was posed with the question of stacking cannonballs on ships by Sir Walter Raleigh on their expedition to America.[22]

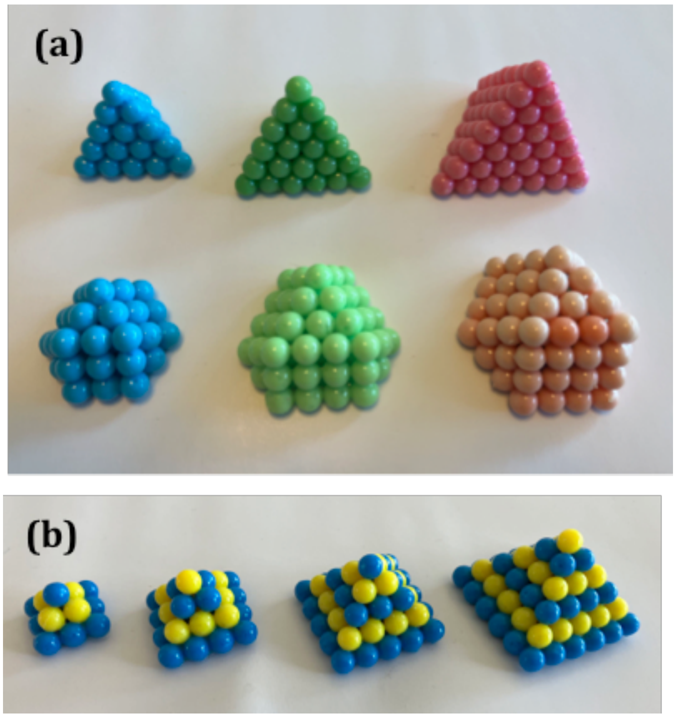

Fig. 3 Physical sphere-in-contact models of (a) NP with triangular (top row) and hexagonal (bottom row) base and (b) NP with a square base.

The piling of cannonballs was then done in a hexagonal or triangular wooden frame forming a six-sided pyramid with a hexagonal base or a three-sided pyramid with a triangular base. Both these NPs are shown in Fig. 3(a). Piling the balls in a square frame results in a four-sided pyramid with a square base, shown in Fig. 3(b). The stacking sequence in these NPs is ABAB, indicated by the blue and yellow color of the spheres. It is therefore obvious that one can color-code the various layers of these nanoparticles in order to show stacking sequence results in face-centered cubic (FCC) and which in hexagonally-closed packed (HCP) lattices. In these close-packed models, the NP with the square base and the triangular base form FCC lattices whereas the ones with the hexagonal base form HCP lattices. The concept of using spheres to model the structure of solids is not new and was published first in the writings of prominent crystallographer Sir William Bragg in the book, “Concerning the nature of things” in 1925. Here he shows that the cubic and hexagonal structure of solids can be modelled by spheres in contact and that the crystal of bismuth can be modelled by spheres with flattened sides.[5]

Recently, magnetic molecular models have appeared that bind spheres with flattened sides in order to model the 3D structure of organic molecules.[23] These molecular models are based on the model suggested for ethane which used tiny bar magnets in the atoms and could be used to measure the rotational potential energy due to the rotation of the C-C bond. [24]

We have built the first sphere-in-contact model of graphite during CDZ PhD between 2001-2005 using marbles and epoxy glue and plexiglass to support the layers, a picture of which is shown in Fig. 4. [25,26]

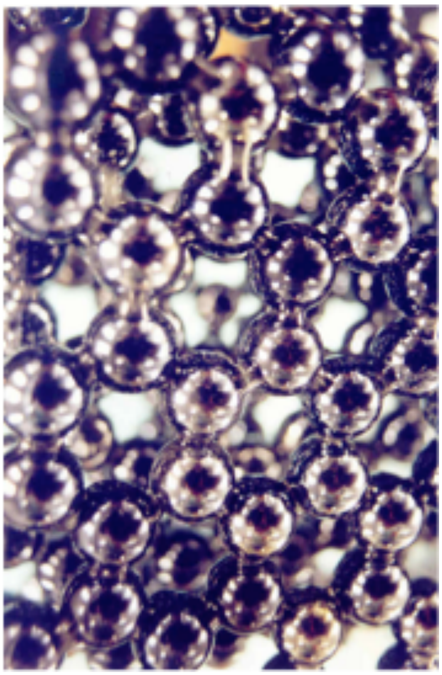

Fig. 4 Picture of sphere-in-contact model of hexgonal graphite built during the doctoral studies of CDZ while in the joint doctoral program between San Diego State University and University of California, San Diego. Materials: black marbles (1.4cm radius) epoxy glue and plexiglass. Picture taken from doctoral thesis presentation done in January 2006.[25,26]

A more extensive model of carbon materials came in a publication in the Journal of Molecular Modeling where we used the sphere-in-contact model to model various carbon materials such as carbon nanotubes, graphene, graphite and fullerene. [11] These models were later used in research to elucidate with the help of DFT calculations the cap structure of the

(3,3)-CNT, (4,4)-CNT and (5,5)-CNT, which was the first use of physical sphere-in-contact models to answer questions concerning the stucture of nanomaterials. Furthermore, a sphere-in-contact model of rhombohedral graphite was used to explain how it could be used as a X-Ray filter.[15]

The sphere-in-contact model for metal NPs supported on (111) surfaces suggests (see Fig. 5(a)-(b)) that there are two types of interfaces that the hexagonal NPs form on (111) surfaces of metals. Three sides of the metal NP have (100)-like sites and the other three have (111)-like sites. These sites can switch easily according to this model by movement of the NP in the direction that is along the 3f-3f path by √3d/2, where d is the diameter of each sphere. The trigonal base NPs on the other hand, (see Fig. 5(c)-(d)) only forms (111)-like sites at the interface between the NP and the (111) surface or only (100)-like sites when the NP is moved in the direction of the 3f-3f path by √3d/2. These results suggest that the interface of the NP/substrate can change significantly structure upon motion of the nanoparticles which can happen during thermal annealing of the catalyst or due to sintering.[27] This motion depends on the total cohesive energy the NP has with the surface, which depends on the size of the NP facet and the type of metal atoms bonded. We estimate that this switching of the catalytic sites will be only observed for small NP by techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM) and high-resolution tunneling electron microscopy (HRTEM). Also transition metals such as Au that have a filled d-orbital will tend to form weaker metal-metal bonds at the interface making the occurrence of this shift more probable. This property of the nanoparticle may find applications in nanotechnology as one could think of magnetic switches change direction of the magnetic field emitted from the NP based on its position, as some of the magnetic properties will change upon switching from (100) to (111) sites at the interface.

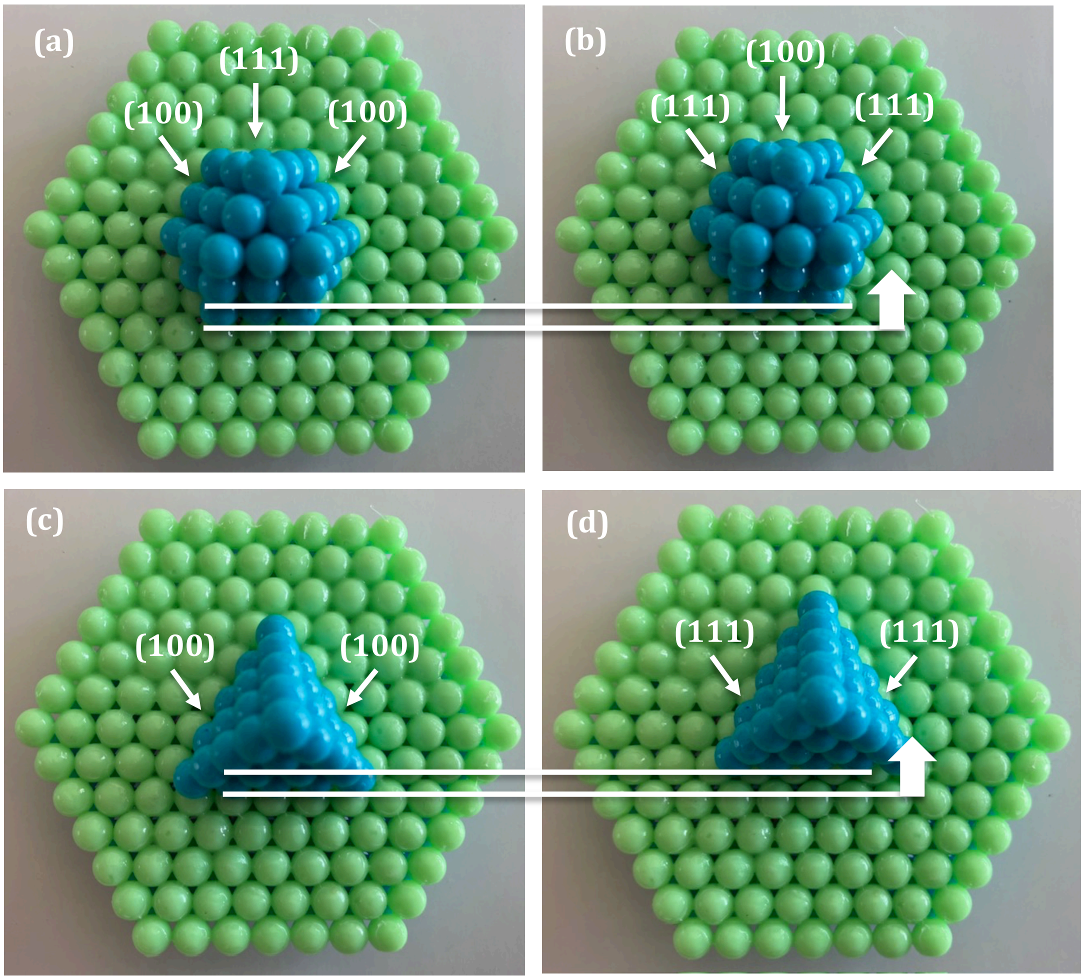

Fig. 5 (a) NP with hexagonal base desposited on flat (111) hexagonal surface (b) shifted by distance between 3f-3f = $\sqrt{3}d/2$ in the vertical direction shown by the thick white arrow. (c) NP with trigonal base deposited on flat (111) hexagonal surface (d) shifted by distance between 3f-3f = $\sqrt{3}d/2$ in the vertical direction shown by the thick white arrow. Where d is the diameter of the sphere.

2.2 Sphere-in-contact model of adsorption on cubic and hexagonal surfaces

This model can correctly describe the structure of ionic lattices and metaloxides as long as these have a cubic or hexagonal structure, due to the templates currently offered commercially which are either square or hexagonal. Fig. 6(a) shows the cubic lattice of sodium chloride and two water molecules adsorbed to it. The sodium is purple and the chloride is green, which are the correct color codes for these atoms according to the CPK model. Also the water molecules the oxygen is red and the hydrogen is white. A limitation of the current model is that it does not take into account that the chloride ion has a larger radius than the sodium ion. The models would be more realistic if there was a different radius for different elements and for their cationic and anionic states. We expect that in the future, additional templates for the grid will become available so that more structures of solids can be modelled. We also expect that sphere-in-contact models will become available that use atoms of different radii in order to get the correct scale as well as angles according to the crystallographic structure.

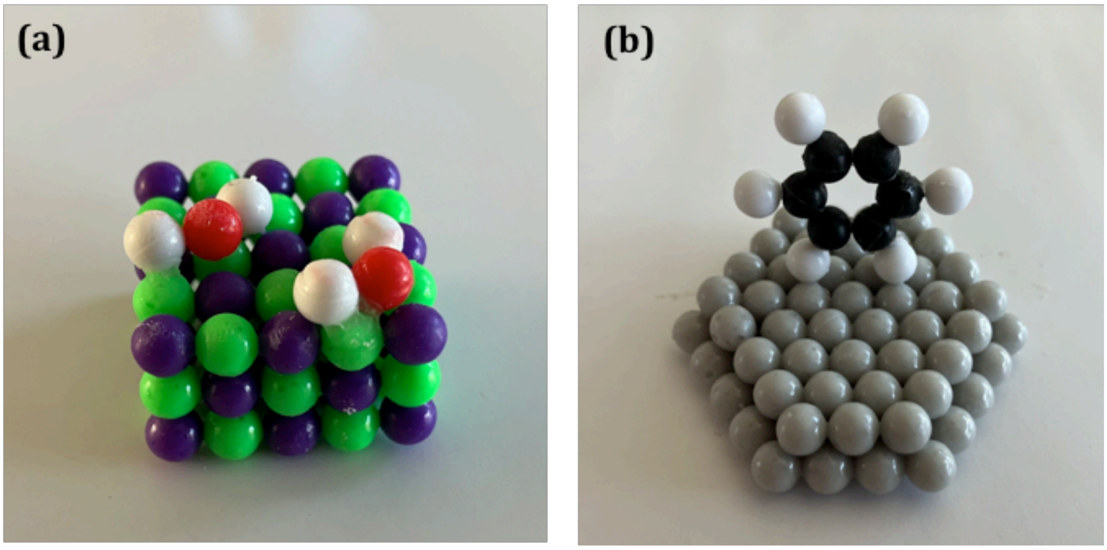

Fig. 6 (a) adsorption of two water molecules on cubic sodium chloride NP (b) Edge-on adsorption of benzene on Pt(111) surface

In Fig. 6(b) we show a sphere-in-contact model of benzene adsorbed edge-on on the (111) surface of platinum. The adsorbed hydrogens are overestimated in size, but one can still see that the hydrogen will adsorb in the 3-fold hollow on (111) surfaces in contrast with what is generally known for the face-on adsorption of benzene on (111) metal surfaces.[28] One can therefore design new structures of adsorbate/substrate systems easily by means of changing the stacking of adsorbates, easier that it can be done computationally. Such new materials with difference stacking of polycyclic aromatic hydrocarbons can be modelled easily with these physical models and may become important in the design of new technological applications such as photovoltaics.

2.3 Sphere-in-contact Model of metal-supported catalysts

The model can correctly show the adsorption geometry of adsorbates on the metal nanoparticle that are supported on various surfaces such as hexagonal graphite and cubic metaloxides. For example, in the ammonia synthesis reaction depicted in Fig. 7(a) on a metal nanoparticle supported on graphite, one can see the reactants of the ammonia synthesis reaction N_2 and $3H_2$ being molecularly adsorbed at the corresponding (100) and (111) surfaces of the metal NP. It shows that N_2 prefers the activation at the (100) facet of the nanoparticle whereas H_2 chemisorbs both at the (111) and (100) facets of the metal nanoparticle, these details are hypothetical but can be explicitly determined in these physical molecular models. The nanoparticle geometry is also explicitly determined as being the one given for FCC or HCP lattices. This model can consider also other NP geometries as long as it can be described by sphere of equal radius that are in contact.

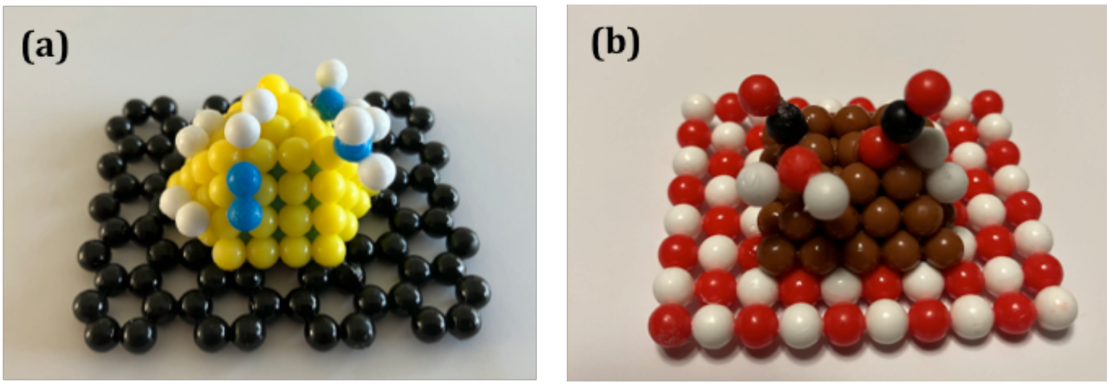

Fig. 7 Sphere-in-contact model of (a) ammonia synthesis reaction over metal core-shell NP supported on a graphene sheet that belongs to graphite. (b) Water-gas shift reaction happening over a Cu_{50} FCC nanoparticle supported on cubic magnesium oxide.

One of the limitations of this model is the relative volume that the hydrogen atom has. For example, it is hard to show properly atomically adsorbed H-species that are on adjacent sites as the spheres are in contact on adjacent 3-fold-hollow/3-fold-hollow (3f-3f), 4f-3f and 4f-4f sites. Furthermore, in the edge saturation of a graphene nanoribbon the carbon-hydrogen bond length seems articfically elongated. The adsorption of the products of the ammonia synthesis reaction can also be correctly depicted with ammonia adsorbed either at a top, bridge or three-fold hollow position. These shortcomings will be resolved by using spheres of difference radius in the future, especially for hydrogen.

Fig. 7(b) shows a Cu_{50} FCC nanoparticle adsorbed on a cubic magnesium oxide (100) surface. The sphere-in-contact model depics accurately the structure of the metal nanoparticle interface which results in a stable (111) like interface. Water and CO are adsorbed on a top and bridge copper site, respectively. The products of the reaction CO_2 and H_2 are adsorbed on a 4-fold hollow (4f) and 3f-3f site, respectively. One can think of such physical molecular models that can be built and in which reaction intermediates are also shown.

2.4. Sphere-in-contact model of various molecular structures

Physical molecular models come in various forms, ranging from simple ball-and-stick models to more complex representations that incorporate different colors, sizes, and materials to highlight specific features of molecules. These models are typically constructed using a combination of atoms and connectors, where atoms are represented as spherical objects, and connectors represent chemical bonds between the atoms. By manipulating the models, scientists can explore the flexibility, chirality, and stereochemistry of molecules. CPK models, also known as Corey-Pauling-Koltun models, are a widely used type of molecular model that represents the three-dimensional structures of molecules. They were developed by Linus Pauling, Robert Corey, and Robert Branson Koltun in the early 1950s and are perhaps the most important molecular models used in organic chemistry. Recently, commercially available sphere-in-contact models of organic compounds have become commercially available in which the atoms bind together by magnets. Ball-and-stick molecular models that use magnets have been previously used by us to elucidate the active site geometry of catalysts in FCC and HCP crystals. From this study it became evident that the use of physical molecular models to study this question had some advantages compared to the use of computer simulations.[29]

The picture in Fig. 8 depicts the sphere-in-contact model of naphalene, ethene and methanol. It shows clearly the basic connectivity between the atoms and the type of the atoms, black being carbon, red being oxygen and white being hydrogen. The model can also show accurately the angles between the atoms. The only disadvantage is that when using spheres of the same size it cannot show correctly the bond lengths. For example in the current models the C-H or O-H bond length is overestimated. We are in the process of developing more accurate sphere-in-contact models in which the bond length of the atoms is to scale.

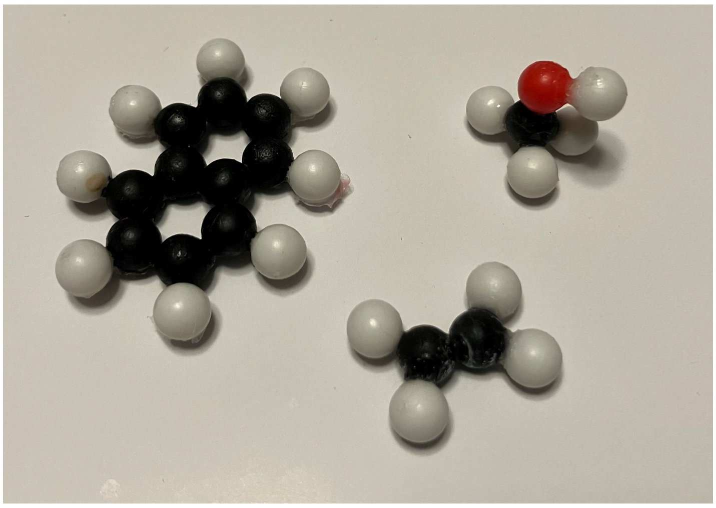

Fig. 8 Sphere-in-contact models of naphthalene, ethene and methanol. Carbon is shown in black, oxygen shown in red and hydrogen shown in white.

3. Conclusions

The sphere-in-contact model provides a simplified yet insightful approach for modeling heterogeneous catalysts and metal nanoparticles. We show that these models can predict the NP/interface structure in terms of (111):(100) sites by movement of the NP on the metal surface. It shows the atom connectivity and can reveal the structure of the metal nanoparticle and the interface between metal nanoparticle and substrate. While limitations exist in the type of models that can be currently build with this current model that uses same radius spheres for all atoms, more advanced models can be envisioned that have the correct color coding for the elements as well as proportions that are in scale for the different elements.

Declarations

Funding: The author declares that no funds, grants, or other support were received during the preparation of this manuscript.

Conflicts of interest/Competing interests: The author has no relevant financial or non-financial interests to disclose.

Availability of data and material: The datasets generated during and/or analysed during the current study are available from the author on reasonable request.

Code availability: No computational tools were used in this study.

Authors' contributions: This study was conceived, designed by Dr. Constantinos Zeinalipour-Yazdi. Both DPP and CDZ collected the data; did the analysis of the models and wrote the paper.

Acknowledgements

The authors would like to acknowledge the companies that offer the beads and template with which these models were built and Sir Prof. Richard Catlow for useful discussions.

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Graphical Abstract