Computational and Theoretical Chemistry 1127 (2018) 8–15

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Viewpoint article

A DFT study on the catalytic ability of aluminum doped graphene for the initial steps of the conversion of methanol to gasoline

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ARTICLE INFO

Article history:
Received 3 December 2017
Received in revised form 2 February 2018
Accepted 2 February 2018

Keywords:
Surface
Graphene
DFT
Energy
MTG
Catalyst

ABSTRACT

The detailed mechanisms for the initial steps of methanol to gasoline (MTG) process, up to 3-carbons products, were studied using DFT calculations and aluminum doped graphene (AG) as catalyst. During the study, the structures of the reactants, products, intermediates and transition states were optimized and confirmed by frequency and IRC calculations. The most of steps are energetically affordable with acceptable barrier energies. The best route (by considering both thermodynamic and kinetic values) was producing ethanol as intermediate and 1-propanol as 3-carbons product. In addition, the production of dimethyl ether and ethylene as intermediates and methyl ethyl ether as a product were energetically possible. This work proved the catalytic ability of AG for MTG process and the results could be employed in the future experimental studies regard to the developments of new catalysts for MTG process.

1. Introduction

During recent centuries, fossil fuels such as coal, oil and natural gas have been the major sources of energy and it is expected that all reserves of fossil fuels will be ended in maximum 200–300 years [1]. Moreover, beside the important role of oil in the energy area, it has been used for production of a wide range of petrochemical products, which they are intermediate products for various industries. Therefore, the development of new technologies for conversion of natural resources (such as coal, gas, etc.) to liquid fuels or other petrochemicals has been highly attractive. One of the most important industrial way for the production of oil is the conversion of methanol to gasoline (MTG) process.

In 1970s, the MTG process discovered by a research group at Mobil Co. (an international oil and gas company) during the conversion of methanol to other oxygen-containing compounds with longer chain using zeolite (ZSM-5) as catalyst [2], while they obtained unexpected hydrocarbons. After this discovery, some countries selected this process as an important way for preparation of gasoline and several companies and research groups have tended their attentions to develope this technology [3,4]. Since discovering, this process has been known as the first and the most important commercial method for the synthesis of gasoline [5]. Therefore, the MTG process has become exclusively important approach as appropriate alternatives for fossil fuels. In this context, understanding the mechanism and developing new catalysts for this process were attractive subjects for the scientists. However, despite many industrial and scientific researches about the general aspects of MTG process, only a few studies about its mechanism have been reported [6–8] and the details of MTG's mechanism remain unresolved. Moreover, among various possible catalysts, the catalytic potency of zeolites has only been defined for this process and developing new catalysts for this process is necessary yet.

Recently, heteroatom-doped graphenes or carbon nanotubes (CNTs) have been used as catalyst in several reactions [9–11]. After the discovery of graphene and especially after the endowment of physics Nobel prize in 2010 to Andre Geim and Konstantin Novoselov for "ground breaking experiments regarding the two-dimensional material graphene", the graphenes and related materials have been placed in the center of attentions [12]. Because of the importance of graphenes in simple and doped forms, they have been used in various applications such as biological purposes [13–17], electrocatalysis [18], DNA sensing [19], high resolution electron microscopy [20], spintronics [21,22], flexible electronics [23,24], bio culturing [25], desalination [26], electronics [27–30], photonics [31], nanoelectronics [32], biosensors [33], super capacitors [34], drug delivery [35,36], H_2 storage [37], transistors [38], polymer nanocomposites [39,40] and fuel cells [41]. It seems that the researches related to the applications of simple and doped graphenes are endless because of their long range and delocalized

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https://doi.org/10.1016/j.comptc.2018.02.001
2210-271X/

π-conjugation and their outstanding electrical, mechanical and thermal properties [42,43]. Moreover, doping of graphene with different heteroatoms has higher sensitivity toward different molecules and let the scientists to develope its applications [44–48]. In this line, theoretical studies proved that the replacement of carbon atom by dopant atom could enhance some of its applications (such as catalytic application) [49–51]. Therefore, in continuation of our previous studies related to the synthesis and applications of doped graphenes [52,53] and since it has proved that computational studies are useful tools to study of the reactions mechanism [54,55], we have decided to develope the possibility of doped graphene as a potential catalyst for the initial steps of the MTG process using computational methods. In this line, full theoretical studies about the details of possible mechanistic pathways of this process could be developed to clarify this method and provide more evidences about its circumstances. Among various heteroatoms, aluminum has shown appropriate properties as dopant atom and aluminum-doped graphene (AG) could be a potential candidate for this purpose [56–60]. Noticeably, the possibility of metal doping in these nanostructured materials has been proved [61]. Aluminum and its compounds are well known as Lewis acids because of the defect in its Lewis structure. Moreover, it plays important role in the catalytic activity of zeolites that have successfully employed as a catalyst in the MTG process.

In this investigation, high-accurate DFT calculations were employed to investigate the catalytic ability of AG in MTG process. Moreover, the energies of all intermediates, thermodynamic and kinetic properties of all steps via various mechanistic pathways, the molecular orbital properties for all species (HOMO and LUMO energies), their energy gap (Eg) and chemical potential (μ) have been calculated. The results of these calculation and the related details will be presented in the following sections.

2. Computational method

All calculations related to the MTG process have performed using Gaussian 09 package [62]. For these calculations, density Functional Theory (DFT) has been employed and among various DFT method, optimizations of all structures and calculation of molecular properties were carried out using M06-2X/6-311G* level of theory because of the high potencies of M06-2X method in the calculation of reaction mechanisms and thermodynamic values [63,64]. M06/2X xc-functional has the extra functionality that are necessary for the investigation of long-range interactions and gives reliable results in the study of systems involved with non-covalent interactions that such these interactions are common phenomenon in this study [65,66]. It should be noticed that although M06-2X method has extreme portion of HF energy, we believe that the results are correct within the constraints, based on our experiences and the reported previous investigations [67–69]. Surely, other methods (such as DFT-D or vdW-DF) could produce the reliable results, as the employed method. The structure of each transition state was obtained using Schlegel's synchronous transit-guided quasi-Newton (QST3) method, starting from the optimized structures of the reactants and ending on the optimized structures of products. Observing one imaginary frequency confirmed that the found structure is transition state (first order saddle point). Moreover, intrinsic reaction coordinate (IRC) calculations proved that each reactant linked to the correct product via allocated transition state. All thermodynamic values (such as Gibbs free energies) were extracted from the results of harmonic frequency calculations at standard conditions (room temperature and atmosphere pressure, STP). Finally, the population analyses were done to obtain the molecular orbital properties and the reactivity parameters (the results of these calculations were moved to the supporting information).

3. Results and discussion

The selection of doped graphene is because of the high specific surface area of graphene and its derivatives. It should be noticed that the common catalysts for MTG process are zeolites, because of their porous structure and existing active cites. However, the specific surface area is important parameter in the catalytic activity and graphenes (simple and doped) are appropriate candidate for this purpose because of their high specific surface area (normally between 300 and 1000 m^2/g) [73,74], which are comparable with or higher than zeolites (between 100–700 m^2/g for different types of zeolites) [75]. Moreover, it was proved that modified (doped) graphenes have enough active cites and could catalyze some chemical reactions. The possibility of conversion of methanol to gasoline (for initial steps) using AG as a catalyst and via different mechanistic pathways has been considered in this work. The employed model for AG was consisted of 42 carbon atoms, 1 aluminum atom and 17 hydrogen atoms for the saturation of all ends (totally 60 atoms). For the insertion of aluminum to the structure of graphene, only one carbon of the graphene was replaced with aluminum and the produced structure was optimized. This optimized model (AG) has employed as a catalyst during the initial steps of the MTG process. The general procedure for the whole process, consisting all reactions, intermediates and transition states, was shown in Fig. 1. This process was started from AG and methanol and ended to AG, water molecules and the carbon-containing products consisted 2–3 atoms of carbon (such as ethylene, ethanol, dimethyl ether, propanol and methyl ethyl ether). All of these intermediates are known as the major low-carbon intermediates of the MTG process [70–72].

The whole process (as shown in Fig. 2.) is consisted of 19 intermediates (named as I1 to I19) and 8 related transition states (named as TSa-b, showing the transition state between intermediates No. a and b). In some steps, it was difficult to find an appropriate transition state. Therefore, we have not reported the structures or energies of these transition states. For more clarification, intermolecular interactions between AG and each species have defined by dotted lines and covalent bonds have defined by solid lines. At the starting point of the work, the structures of AG and all small molecules (water, products and intermediates without AG) were optimized and then, the structures of all intermediates were optimized. The graphical pictures of the optimized structures of all intermediates were shown in Fig. 2.

After the optimization of all intermediates, finding and optimization of the transition states between them is important. Therefore, we have found, optimized and confirmed the structures of the most of transition states during the MTG process. It should be noticed that to reduce the computational cost of this study, the structures and energies of some transition states were not studied, consisted of physical adsorption processes (which normally have small barriers) and some final steps that had the same chemical processes with the previously calculated transition states. During this part of study, some changes have been made on the structure of intermediates (the final intermediates have been considered and reported) and various transition states have been considered to obtain the final transition states. The structures of all of these transition states were shown in Fig. 3.

As showed in Fig. 2, by doping of aluminum into the structure of graphene, despite the larger atomic radius of Al versus C, the graphene structure was not deformed from the planar structure. All C—Al bond lengths in the optimized structure were 1.745 Å. This value is remarkably less than the bond length of common C—Al