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A DFT method analysis for formation of hydrogen rich gas from acetic acid by steam reforming process

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ABSTRACT

Quantum chemical calculation has been considered for molecular behaviour analysis during hydrogen production through steam reforming process of acetic acid is an organic compound and the simplest carboxylic acid. Hydrogen and also Carbon dioxide are the products when acetic acid reacts with water. Geometry optimization for individual molecules (CH_3COOH, H_2O, H_2, and CO_2) was carried out using DFT/B3LYP method in Gaussian 09 W computational chemistry program based on 6-31G(d) basis set along with the consideration of reactant side (two molecules together) and product side (two molecules together). Several fundamental features for optimized geometry such as bond angle, bond length and also the minimized energy values have been computed. The method has been compared with other literatures for validation. The nature of the chemical conversation in terms of electron flow, ionisation potential (I) and electron affinity (A) between acetic acid and water has been investigated via HOMO–LUMO energy values and gap. Interaction energies of reactant along with product side and some essential properties in quantum chemical application; chemical potential (μ), the global hardness (η) and softness (S), electrophilicity index (ω) as well as electronegativity (X) have also been calculated and analyzed.

1. Introduction

Energy is the vital fact for expansion and development of the modern civilization. With growing challenge of environmental issues and because of the energy crisis, specific clean and renewable energy sources are expected as the substitute of conventional energy sources. For the rising demand of clean and new energy, hydrogen is accepted as the ideal energy carrier to continue sustainable energy growth which is non-polluting and efficient energy vector [1]. The substitution of fossil fuel systems by using hydrogen (H_2) energy systems would be the best solution [2]. H_2 is the most abundant gas in the universe. It is lighter than air. It can easily be used as feed in fuel cells for generating clean and high efficient power. The only by-product of hydrogen is water [3]. Hydrogen (H_2) reacts with oxygen (O_2) to form water (H_2O) and releases energy. The energy released allows hydrogen to act as a carbon free fuel which has energy content per unit weight of 142 kJ/g [4,5]. It has high specific energy (~120 MJ kg^{-1})[6]. During the combustion of hydrogen, three times higher quantity of energy (39.4 kWh kg^{-1}) has been produced than the production of any other fuel on a mass basis, e.g liquid hydrocarbons (13.1 kWh kg^{-1}) [7]. Therefore, hydrogen is considered the most promising in the succession of fuel evolution.

Acetic acid (CH_3COOH) is an organic compound which is a colourless liquid with unique sour taste. It is the second simplest carboxylic acid and is a crucial chemical reagent. Acetic acid that can be found in bio oil around 12 percent, is one of the key elements of bio-oil [8]. Hence, it has been considered as the major compound for this quantum chemical study. At present, steam reforming is a promising approach for generating hydrogen rich gas, carbon monoxide and other beneficial products from the hydrocarbon. Steam reforming of acetic acid is completely feasible from the thermodynamic point of view [9,10]. The reaction is endothermic [11]. There are a couple of options to deliver heat to this reaction system. The first one is externally, which is by burning up fuel and carrying heat directly into the reaction mixture. The second one is internally, which is by co-feeding air or oxygen and burning up a part of acetic acid and complete conversion is accomplished at around 350 °C [10]. The aim of steam reforming reaction of acetic acid is to produce just as much hydrogen as possible. The overall steam reforming reaction of acetic acid is [11–14],

$$CH_3COOH(l) + 2H_2O(l) \rightarrow 2CO_2(g) + 4H_2(g) \quad (1)$$

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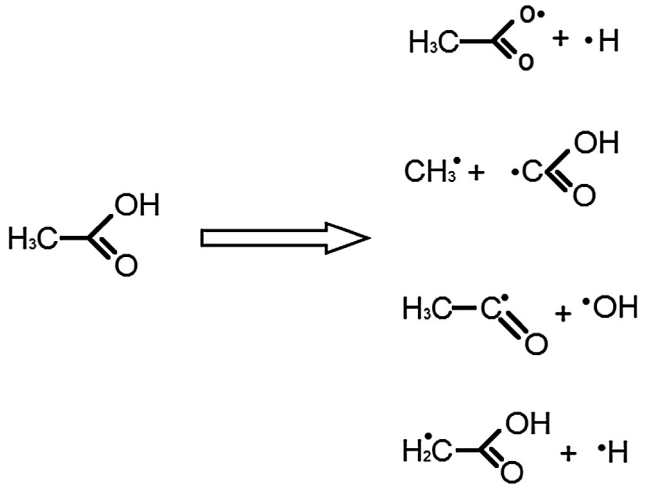

Fig. 1. Possible decomposition pathways of acetic acid [12].

Basagiannis et al. [11] pointed out the catalysts effect on acetic acid during the steam reforming reaction for hydrogen production. Their findings clearly showed that homogeneous reaction obtained at temperature 850 °C with the presence of Ni-, Rh- and Ru-containing catalysts. Pd and Pt catalysts showed much lower activity. Chen et al. [14] also performed an experiment to point out the process for H_2 production. They also introduced a method to produce hydrogen by electrochemical catalytic reforming of acetic acid over the 18% NiO/Al_2O_3 catalyst at relatively low temperature of 300–400 °C. Mohanty et al. [13] discussed about the hydrogen production by catalytic steam reforming (CSR) of biomass-derived oil which contains 12–14% acetic acid. The maximum hydrogen yield was 80 percent that could be achieved at temperature 800 °C. They all showed that the decomposition of compound in steam reforming process starts at high temperature (300 °C to 900 °C). The possible decomposition pathways of acetic acid to produce hydrogen have been shown in Fig. 1 [12].

Quantum chemistry is really a promising area of chemistry. Presently quantum chemical calculations are being widely used in diverse areas of chemistry to forecast activity of molecules prior to experiment [15]. It helps to predict molecular behaviour in terms of energy change and electronic behaviour during the reaction. Density Functional Theory (DFT) is a quantum chemical approach that has been used to analyse this steam reforming reaction of acetic acid to know the actual nature of the reaction. Important quantum chemical parameters such as geometry optimization, HOMO–LUMO energy and gap, global hardness and softness, Electronegativity, electrophilicity index, interaction energy and chemical potential are really important to analyze the nature of this reaction. DFT method has extensively used in chemical reaction for the interpretation and prediction of complex system behaviour at an atomic scale. DFT is primarily a theory of electronic ground state structure. DFT is preferred for dealing with the several atoms and when a modest accuracy is needed [16]. There has been in recent years a sharp increase in the number of molecular electronic structure calculations based on DFT method [17].

The previous study shows that many researchers used the acetic acid for hydrogen production by steam reforming process but they did not consider any quantum chemical approaches to know the activity of molecules, energy changes and electronic behaviour. To the best of the authors' knowledge, quantum chemical method has been considered to investigate the molecular behaviour analysis for production of hydrogen from acetic acid through steam reforming process. The stable geometric structures are optimized by DFT method and analyzed the structural parameter and minimum energy value. Energetic behaviour is studied by investigating the HOMO–LUMO energy values and their gap indicates the molecular stability which is also important to know the nature of the reaction. Electronegativity (X) and electrophilicity index (ω) also represent the energetic behaviour which is also known from the HOMO–LUMO energy. Therefore hydrogen formation from acetic acid by steam reforming process is investigated in the point of electronegativity (X) and electrophilicity. Previous study indicates that interaction energy represents the energy change so this can be used for the acetic acid too. Chemical potential is also used to know the electron flow in the reaction.

2. Background theory

Geometry optimization is a crucial portion in application of quantum chemical calculation in concern of several aspects [18]. Geometry of a molecule ascertains many of its physical and also chemical properties. The main objective of geometry optimization is to obtain an atomic arrangement which usually makes the molecules most stable. The energy is minimum when the geometry is optimized [19]. The initial geometry and the coordinate system are the essential aspects for the effectiveness of the optimization of molecule [20]. Energy calculation is the vital part in case of geometry optimization of a molecule. Total molecular energy, thermal energy, gibbs free energy, HOMO–-LUMO energy and also enthalpy can be calculated once the geometry is optimized.

HOMO and LUMO values assist to demonstrate the kinetic stability and chemical reactivity of the molecule [21]. In general, HOMO has the capacity to donate an electron and it estimates the negative ionisation potential (I) [22]. LUMO stands for electron acceptor along with a good estimation to the negative of electron affinity (A) [22]. The energy of HOMO is linked to the ionisation potential (I) while the energy of LUMO is used for estimation of the electron affinity (A) in an approach shown by the Hizaddin et al. [23] and Zhan et al. [24] in which ionisation potential (I) is − ϵHOMO and electron affinity (A) is − ϵLUMO. The HOMO and LUMO energy gap is usually figured out from the difference in HOMO and LUMO energy values. The difference indicates the molecular stability [25]. A large HOMO–LUMO energy gap indicates high stability for the molecules have low reactivity [26]. For a low reactive molecules, it is difficult to accept electrons to the high-lying LUMO as well as take out electrons from the low-lying HOMO [27]. A small HOMO–LUMO energy gap indicates the low stability of molecule. Therefore, the molecules are highly in chemical reaction. Some essential quantum chemical parameters for instance chemical potential (μ), the global hardness (η) and softness (S), electrophilicity index (ω) and electronegativity (X) have been calculated and discussed by Hizaddin et al. [23]. All these parameters can be calculated from HOMO and LUMO energy values.

Since the Hardness and Softness are directly related to the HOMO and LUMO energies, hence these two are good indicators of chemical stability [28]. Soft molecules need smaller energy to be excited compared to hard molecules. Hizaddin et al. [23] and Pearson [29] pointed out that the global hardness is directly related to the HOMO and LUMO energy gap by the following expression,

$$\text{Hardness};\eta = \frac{\varepsilon LUMO - \varepsilon HOMO}{2} \tag{4}$$

Pearson [30] and Parr et al. [31,32] pointed out that the reciprocal value of the hardness is softness, which usually measures the easiness of transferring the charge as well as it is related to higher polarizability [33],

$$\text{Softness};S = \frac{1}{\eta} \tag{5}$$

The Electronegativity (X) is the capability of any molecule to attract electrons [34,35] and Pearson et al. [36] demonstrated this by the following expression.

$$X = \frac{I + A}{2} = \frac{-\varepsilon HOMO - \varepsilon LUMO}{2} \tag{6}$$