

Theoretical study of ethanol partial oxidation for syngas production under cold plasma conditions



Wenju Wang^{a,*}, Yingyu Cao^{b,c}

^aSchool of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

^bSchool of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^cCollege of Chemistry and Life Science, Tianjin Normal University, Tianjin 300387, China

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ABSTRACT

In this work, pathways of partial oxidation of ethanol under cold plasma conditions have been studied by density functional theory (DFT) method. The calculation results show that the energy barrier of ethanol conversion is reduced and the conversion from ethanol to H₂ and CO is promoted with the presence of O₂ under cold plasma conditions. The formation of syngas is through a multi-step pathway via the methoxy radical conversion and dissociation of formaldehyde, while the recombination of H generated extra H₂. The present DFT study also demonstrates that the plasma synthesis will normally lead to a formation of a mixture of syngas, hydrocarbons, and oxygenates.

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1. Introduction

Ethanol (C₂H₅OH) has been recently recognized as a promising alternative fuel [1], it can be produced through the fermentation of biomass or renewable raw materials, including energy plants, waste materials from agro-industries or forestry residue materials, organic fraction of municipal solid waste, etc. Therefore, the C₂H₅OH-based energy conversion system has the significant advantage of being nearly CO₂ neutral (no net releasing of carbon dioxide into the atmosphere) [2]. In addition, C₂H₅OH is easier to handle, store and transport in a safe way due to its lower toxicity and volatility.

C₂H₅OH can be converted into syngas through steam reforming (SR) [3–8], partial oxidation (PO) [9–13], and autothermal steam reforming (ATR) [14] and dry reforming [15]. Almost all the reported syngas production from C₂H₅OH is via steam reforming, partial oxidation, autothermal steam reforming or dry reforming over noble metal (e.g. Pt, Ru and Rh) or transition catalysts (e.g. Ni, Co and Fe) at 800–1000 K. Obviously, the catalytic ethanol conversion needs a start-up stage and no syngas is generated before the temperature is sufficiently high (>800 K). In this regard, the partial oxidation of C₂H₅OH under plasmas conditions has been proposed.

The cold plasmas have been successfully utilized for the production of ozone (O₃) and have been extensively investigated to convert CH₄ into higher hydrocarbons and syngas [16–19]. The cold plasmas are also promising as a H₂ generation technology. Water (H₂O), CH₄ and methanol (CH₃OH) have been studied as the feedstock [20–26]. The cold plasma partial oxidation can be performed at low temperature (as low as room temperature). The highly energetic electrons within cold plasmas are responsible for the initiation and sustain of reactions. The advantage of cold plasmas is its rapid response without induction period that exists in the conventional catalytic reforming processes. In addition, the plasma C₂H₅OH conversion process is efficient, simple and flexible.

Cold plasma partial oxidation of C₂H₅OH involves many complex reactions, so several intermediate byproducts, such as formaldehyde (CH₃CHO) and ethylene (C₂H₄), are formed and end up in the product. These byproducts are valuable and normally require a lot of steps to be generated but can be easily formed during C₂H₅OH conversion via cold plasma.

As a crucial first step, it is very necessary to understand the reaction pathways of C₂H₅OH partial oxidation under cold plasma conditions. In this work, we attempt to investigate these pathways by a DFT study.

* Corresponding author.

E-mail address: wangwenju1982@gmail.com (W. Wang).

2. Computational details

All the calculations were performed with the DMol³ program from Materials Studio [27–29]. A double numerical plus polarization (DNP) basis set was used to describe the valence orbitals of O, C and H atoms. The accuracy of the DNP basis set has been analyzed in detail by Delly [27]. The Perdew-Wang (PW91) functional of the generalized gradient approximation (GGA) [30,31] was employed to calculate the non-local exchange and correlation energies of reactants, products and some transition states existing in partial oxidation of C₂H₅OH via cold plasmas. All the energy values were determined for 298.15 K. The linear synchronous transit (LST) and quadratic synchronous transit (QST) methods were used to study the transition states [32]. The transition states were confirmed by the nudged elastic band (NEB) method [33].

3. Results and discussion

3.1. Structure parameters

Fig. 1 presents the optimized structures of some species during partial oxidation of C₂H₅OH using cold plasmas and their optimized structures parameters.

3.2. Dissociation of ethanol

There are six dissociation routes for C₂H₅OH that have been studied theoretically [34]:



where e' represents the electrons with less energy. Eq. (1) is an O–H bond breaking progress, and the required energy for this reaction is 107.57 kcal/mol. Eqs. (2)–(4) requires an energy input of 99.25, 97.15 and 101.99 kcal/mol, respectively. Eqs. (5) and (6) have transition states TS1 and TS2, and their activation energies are 59.82 and 72.84 kcal/mol, respectively. Normally, the electron energy within cold plasmas is around 23.05–230.5 kcal/mol. Therefore, these electrons can easily make these reactions [Eqs. (1)–(6)] occur under cold plasma conditions. Among these six C₂H₅OH dissociation routes, Eq. (5) requires the lowest energy, which has been confirmed by other investigators [35].

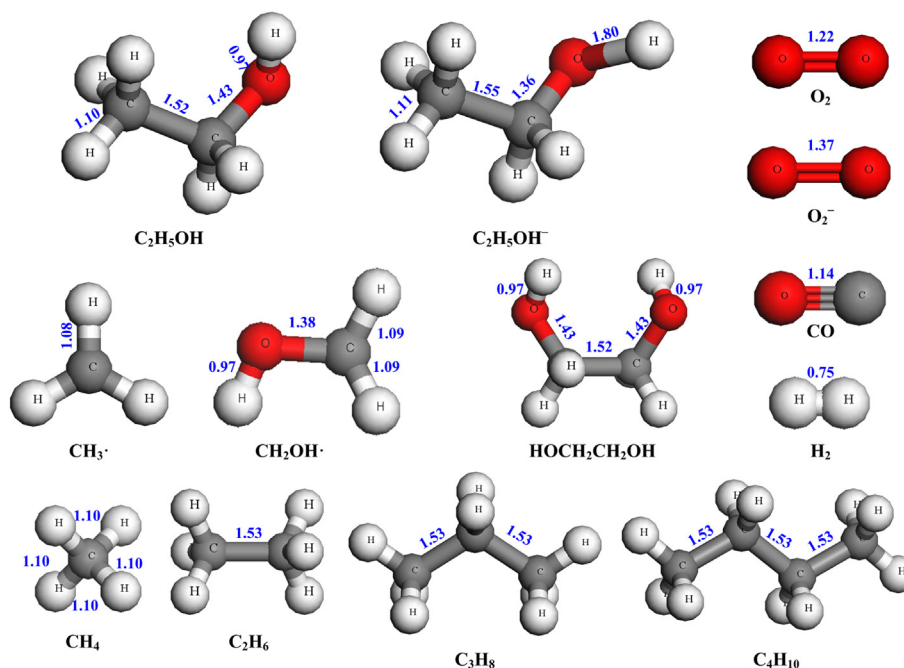


Fig. 1. Optimized structure of some species in partial oxidation process of C₂H₅OH under cold plasma (Bond distances in Å).

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