DFT study of the enhancement on hydrogen production by alkaline catalyzed water gas shift reaction in supercritical water

Runyu Wang, Liejin Guo[*], *Hui Jin, Libo Lu, Lei Yi, Deming Zhang, Jia Chen*

State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi'an Jiaotong University, 28 Xianning West Road, Xi'an 710049, Shaanxi, China

ARTICLE INFO

ABSTRACT

Supercritical water gasification (SCWG) is hopefully to be an acceptable choice for hydrogen production, the hydroxide ion assisted water gas shift reaction (WGSR) has been regarded as the most important reaction to generate hydrogen during the process. However, the principle of practical OH^- catalyzed reaction is not possible to acquire by experiments. Thus, density functional theory (DFT) is utilized to investigate the reaction mechanism theoretically in this work. Through first principle calculations, every species and energy barrier for elementary steps are achieved, and formate ion is determined as the important intermediate. Besides, $HCOO^- + H_2O \rightarrow HCO_3^- + H_2$ is the dominant path to generate hydrogen, as well as the rate-determining step with 47.94 kcal/mol energy barrier. Furthermore, the reaction rate constant is calculated to be $k_{catalytic}(s^{-1}) = 2.34 \times 10^{12}exp(-1.80 \times 10^5/RT)$ using transition state theory with Wigner transmission coefficient (TST/w). Lastly, supercritical water condition is demonstrated to be a favored media for WGSR, because it may dissociate, dissolve or hydrolyze more hydroxide anion than conventional steam. The results are expected to benefit the control of reaction process and the design of SCWG reactor.

Introduction

Hydrogen shows great potential as an ideal alternative energy for its high calorific value per unit mass. Several methods [1—3] have been developed to generate hydrogen, such as solar hydrogen conversion, thermal decomposition, fossil fuel reforming, water splitting [4] and so on. Among these processes, water gas shift reaction (WGSR) [5,6], which has been widely used in industry to generate hydrogen for many years, is usually the key process to generate hydrogen if the carbon

based materials are used. With in situ spectrum analysis, formic acid is observed as the intermediate during reaction (1) [7].

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$
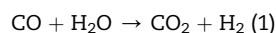
Supercritical water gasification (SCWG) is an alternative way for industrial hydrogen production, this technology is feasible to convert waste [8—10] and coal [11—13] to hydrogen. Supercritical water (SCW) shows advantages for WGSR because of higher water density, and lower energy barrier

---

according to Melius' work [14], but WGSR is still not a fast reaction. The great amount of H_2 needed by the envisioned hydrogen economy, for instance with hydrogen fuel cells [15,16], has motivated interest on proper catalysts to accelerate the important reaction. Most of studies were about metal-based heterogeneous catalysts, experimentally and theoretically. However, the intermediate of heterogeneous catalyzed WGSR has not unified yet, the two mechanisms usually discussed are formate intermediate mechanism and carboxyl intermediate mechanism [17]. On the other hand, the mechanism of homogeneous catalyzed WGSR did not gain enough attention, moreover most of the work focused on metal carbonyl catalysts. Some metallocarboxylic acids and metalloformates may be generated as active intermediates during the processes, then the intermediates decompose into CO_2 and H_2 [18], alkaline condition is found to enhance the homogeneous metal carbonyl catalysis of the WGSR.

Alkalis and alkali salts are frequently added as homogeneous catalysts in SCWG to enforce the reaction process and increase hydrogen production, the base catalyzed WGSR is mostly thought as the reason for the increment [21]. Catalysis of WGSR by aqueous alkaline compounds has been reported long before [19,22−24], the most probable reason is the formation of formate salts during the process. Nevertheless, different mechanisms have been postulated, as are shown in Table 1. Elliott et al. [19] used nuclear magnetic resonance spectrometry to analyze the cooled liquid sample to determine the intermediate of basic catalyzed process, and proposed reaction pathways in scheme II. Sinag et al. [20]also speculated a mechanism of carbonate catalyzed WGSR (in scheme III). Nevertheless, because of the resistless of optical cell (Al_2O_3, SiO_2) under alkaline condition, it is not possible to use spectrum analysis to determine the exact intermediate during the reaction processes, subsequently no mechanism can be summarized.

Research motivation

Achieving an authentic reaction mechanism is essential, because it is capable of providing the theoretical basis to attain appropriate reaction conditions. Therefore, we utilized Density functional theory (DFT) to overcome the limitation of experimental instruments to unveil the simple but opaque reaction. DFT is believed to be useful to investigate the reaction mechanism [25]. It has been utilized to study the heterogeneous catalyzed [26,27], homogeneous metal carbonyl catalyzed [28] and non-catalyzed WGSR [29,30]. The DFT-derived parameters, including energy of barriers, length of bonds, vibration mode, and charge distribution are capable to help to understand the alkaline catalyzed mechanism. With

the parameters, we determined the rate constants of both uncatalyzed and OH^- catalyzed WGSR, which had been fitted into Arrhenius Equation. The accurate kinetic parameters are available in optimizing the utilization of catalysts and the design of reactor.

DFT simulation approach and verification

Calculations were performed using GAUSSIAN 09 programs. The optimization of the reactants and products of every step along the possible pathway was carried out by using the density functional theory (DFT) method B3LYP with 6−311++G(d,p) basis set [31,32], Double diffuse functions were applied for accuracy because of the anions and the molecules with lone pairs. Since negatively charged systems required more flexible basis sets, we chose the 6-311 level augmented with polarization function and diffusion function. Spin unrestricted was used because of the odd number of ions. Strict convergence tolerance was used: convergence of the maximum force was 0.00045 Ha/Å, the value of maximum displacement was 0.0018 Å. All the vibrational frequencies were also obtained at B3LYP/6-311++(d,p) level to determine every stationary points (no imaginary frequencies for the minima geometries of reactants, complexes or products, while only one imaginary frequency for transition states). The Mulliken charge was calculated to analyze the collision method of reactants. After finding transition states, we used intrinsic reaction coordinate (IRC) method to determine the reactant and product of every transition state to confirm the reaction pathway. All the energies were calculated with zero point energy (ZPE) unless otherwise indicated.

We used conventional transition State Theory (TST) with the Wigner transmission coefficient (TST/w) to calculate the reaction rate constants [33]. The Vibration Scaling Factor was chosen as 0.983.

To confirm the validity of the methods used, we calculated the barriers along the reaction pathways of non-catalytic mechanism of WGSR. The minimum reaction pathway of potential energy surface (PES) goes through as the following steps: (1) the combination of CO and H_2O for trans-HCOOH; (2) the transition from trans-HCOOH to cis-HCOOH and (3) the decomposition of cis-HCOOH to CO_2 and H_2. The energy barrier of each step is 58.41 kcal/mol, 13.21 kcal/mol, and 68.89 kcal/mol, respectively. The values in bracket are the barriers without ZPE in Fig. 1. The results of our work are in well agreement with the previous theoretical [30] (69.8 kcal/mol at B3LYP/6-311+G(3df,2p) level) and experimental [34] (65−68 kcal/mol) results. Owing to better agreement with literature when calculated with ZPE, the rest energies in this work will be shown with ZPE. The details of various stationary

Table 1 − Different speculated mechanisms.

Scheme I	Scheme II [19]	Scheme III [20]
$K_2CO_3 + H_2O \rightarrow 2KOH + CO_2$	$2CO + 2OH^- \rightarrow 2HCOO^-$	$K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH$
$2CO + 2KOH \rightarrow 2HCOOK$	$2HCOO^- \rightarrow HCOH + CO_3^{2-}$	$KOH + CO \rightarrow HCOOK$
$2HCOOK + 2H_2O \rightarrow 2HCOOH + 2KOH$	$2H_2O + CO_3^{2-} \rightarrow 2OH^- + H_2CO_3$	$HCOOK + H_2O \rightarrow KHCO_3 + H_2$
$2HCOOH \rightarrow 2CO_2 + 2H_2$	$H_2CO_3 \rightarrow H_2O + CO_2$	$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2$
$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$	$HCOH \rightarrow H_2 + CO$	$H_2O + CO \leftrightarrow HCOOH \leftrightarrow H_2 + CO_2$