Understanding the kinetics of carbon-hydrogen reaction: Insights from reaction mechanisms on zigzag edges for homogeneous and heterogeneous formation of methane

Lucas A. Calderón [a, *], Eduardo Chamorro [b], Juan F. Espinal [a]

[a] Química de Recursos Energéticos y Medio Ambiente, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia
[b] Universidad Andres Bello, Departamento de Ciencias Químicas, Millennium Nucleus Chemical Processes and Catalysis, Facultad de Ciencias Exactas, Av. República 275, 8370146 Santiago de Chile, Chile

ARTICLE INFO

ABSTRACT

Although mechanisms for the methane formation in the carbon-hydrogen reaction ($C + 2H_2 \rightarrow CH_4$) have been proposed from molecular modeling, there is still no compelling evidence about their kinetic feasibility. In this work, we provide evidence about mechanisms for the methane formation in the carbon-hydrogen reaction from a kinetic point of view. Kinetic parameters for all elementary steps were explored within the framework of the density functional theory and the conventional transition state theory from 298 K to 1500 K (at 0.1 MPa). Variation with time of concentration and reaction rates for the species involved in the proposed mechanisms were calculated numerically by solving the systems of ordinary differential equations accounting for the behavior of each species concentration. The proposed mechanisms allow to explain the effect that variation of i) partial pressure of H_2, ii) graphitic degree of carbonaceous materials and, iii) H radical concentration, has on the overall methane formation rate. Moreover, the calculated profiles of reaction rates reproduced qualitatively well the widely experimentally observed sharp decrease of the overall methane formation rate. This decrease is rationalized via the calculated concentration profiles of the species involved in the proposed mechanisms.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon-hydrogen reaction (1) (also known as hydrogasification) is a reaction of interest in several fields and its understanding is fundamental for many clean coal utilization technologies, such as the integrated gasification combined cycle (IGCC) [1] and the zero emission coal (ZEC) [2,3].

$$C + 2H_2 \rightarrow CH_4 \qquad (1)$$

Carbon-hydrogen reaction has been widely studied at temperatures above 1000 K and pressures ranging from 1 MPa to 10 MPa [4—26]. At these conditions methane is the main gaseous product [16,17,20,23,26] but other hydrocarbons are produced in small quantities [5,7,10,16,20—22]. Even though reaction (1) is an exothermic reaction [27], high temperatures are required to

achieve an appreciable reaction rate. Moreover, it has been reported that high H_2 partial pressures promote the carbon-hydrogen reaction by increasing the methane formation rate [8,16,28]. According to previous reports for graphitic carbons [29,30] and coal chars [6,12,31—37], there is a sharp decrease in such rate when conversion increases. Juntgen [38] proposed that this behavior could be attributed to the increase of activation energy with conversion due to the consumption of reactive carbon during the reaction. Toomajian et al. [31] attributed the decline in rate to two reasons: (1) strong adsorption of inactive hydrogen which blocks active sites; and (2) development of unreactive surface structure. This last reason was initially suggested by Pang and Yang [39]. From etch-pit analysis, they found that hydrogen forms hexagonal etch pits on graphite bounded by zigzag edges. Based on theoretical calculations and for a high degree of carbon edge hydrogenation, these authors proposed that zigzag edges are less reactive than armchair edges. Therefore, it was concluded that the decrease in the rate of carbon-hydrogen reaction is due to the decrease in the concentration of the more reactive edge (the armchair edge) at a

* Corresponding author.
E-mail address: lucas.calderon@udea.edu.co (L.A. Calderón).

high hydrogenation degree. A new question emerges when Pang and Yang's proposal is considered to be valid: Does the reaction rate decrease only because of the decrease in the concentration of the more reactive edge at high hydrogenation degree or does it decrease as a consequence of the concomitant decrease of the zigzag edge reactivity?

Recently, we have proposed some mechanisms for methane formation in the carbon-hydrogen reaction (see Fig. 1) [40]. These mechanisms were proposed based on relevant thermodynamic and kinetic information evaluated at 298 K and 1100 K after modeling the elementary reactions with electronic structure methods [40]. Briefly, the elementary reactions can be grouped in five reaction steps, namely reactive sites saturation, edge hydrogenation (to form > CH_2 groups), ring opening (producing methyl groups), desorption of methyl groups (or even direct desorption of methane), and production of methane by homogeneous gas phase reactions of methyl radical with H_2. To provide some support, at least of the thermodynamic feasibility of the proposed mechanisms, the variation of overall state functions was contrasted with experimental evidence from 298 K to 1500 K. Nevertheless, neither the most commonly experimentally reported kinetic aspects of carbon-hydrogen reaction were rationalized nor the overall rate for methane formation was evaluated algebraically or numerically. Thus, our aim in this study is not only to provide evidence about the kinetic feasibility of the previously proposed mechanisms, but also to provide some insight for understanding the strong decline in the reaction rate with conversion.

2. Computational methodology

2.1. Calculation of rate constants for elementary reactions

A detailed description of both the molecular model used and the calculation method have been previously published [40]. All calculations (geometry optimizations, single-point energies, and vibrational frequencies) were performed using the implementation of the density functional theory (DFT) on the Gaussian 09 package [41] at the B3LYP/6-311++G(d,p) level of theory. For carbonaceous models like those used in this work, this choice of model chemistry provides energetic quantities whose quality is reasonably comparable to those provided by the CCSD(T) method [42], and has been usually used in the elucidation of reaction mechanisms involving carbonaceous materials [43,44]. Although this choice leads to a small spin contamination for unrestricted wavefunctions for model structures of carbonaceous materials [45], a careful inspection of its results is required, especially those related with kinetic quantities. For this purpose, two additional functionals were used (M06-2X and ωB97X-D) with the basis set 6-311++G(d,p). These functionals have been recommended in recent benchmarking studies for modeling thermochemistry, kinetics, and non-covalent interactions in systems containing main group elements [46–48].

Rate constants for forward and reverse elementary steps were calculated by using equation (2) provided by the canonical transition state theory [49]. In this equation k_B is the Boltzman constant, h is the Plank constant, R is the universal gas constant, P^0 is the standard pressure, $\Delta G^{0,\ddagger}$ is the standard Gibbs free energy of activation at T, and Δn is equal to 0 or 1 for unimolecular or bimolecular reactions, respectively.

$$k_i(T) = \frac{k_B T}{h} \left(\frac{RT}{P^0}\right)^{\Delta n} exp\left[-\frac{\Delta G^{0,\ddagger}(T)}{k_B T}\right] \tag{2}$$

The relevance of the Eckart tunneling correction [50] was also considered. Unless otherwise stated, all kinetic quantities will be discussed at the B3LYP/6-311++G(d,p) level of theory.

2.2. Calculation of concentration and reaction rate profiles

For every proposed mechanism, the stiff system of coupled non-linear ordinary differential equations (ODE) accounting for the change in time of each species concentration was proposed in accordance to the law of mass action (see Tables S4 and S5 in the Supporting Information). Each ODE system was numerically solved in Mathematica [51]. Given the huge number of molecules involved in the carbon-hydrogen reaction, a deterministic time course simulation of the mechanism using the LSODA solver [52] was followed rather than a stochastic simulation. LSODA solver was used with relative and absolute tolerance values of 10^{-6} and
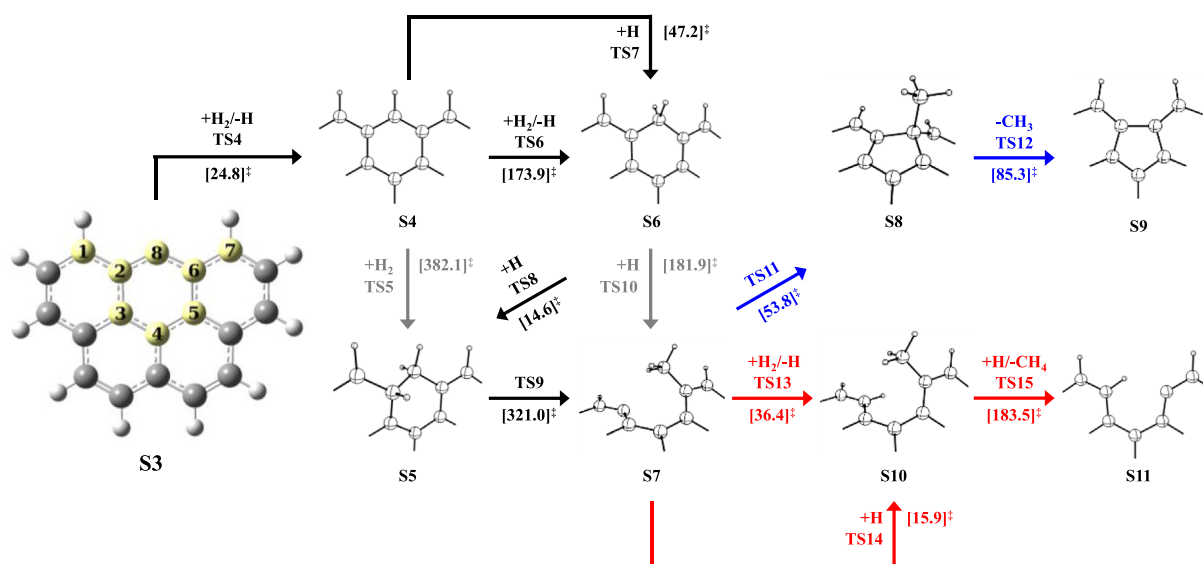

Fig. 1. Previously proposed mechanisms for methane formation in the carbon-hydrogen reaction on the zigzag edge of carbonaceous materials through desorption of methyl group (blue arrows) and direct desorption of methane (red arrows) [40]. For all structures, only reaction region is shown. Activation energies (E_a, square brackets) are given in kJ mol^{-1}. Reprinted from Carbon 102, 390, *Mechanisms for homogeneous and heterogeneous formation of methane during the carbon-hydrogen reaction over zigzag edge sites*, Calderón, L. A., et al., Page No. 394, Copyright (2016), with permission from Elsevier. (A colour version of this figure can be viewed online.)