Numerical Investigation on the Number of Active Surface Sites of Carbon Catalysts in the Decomposition of Methane

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DOI 10.1002/aic.14395

The number of active sites on the surface of carbon catalysts is an important factor in determining their activity in the decomposition of methane. Although several studies have been performed to identify the nature of these sites, no method has been established to estimate their number. A method is presented to estimate this value, and its effect on hydrogen production is evaluated, along with that of temperature and residence time. For this purpose, the thermocatalytic decomposition of methane is modeled with the inclusion of the number of active sites of the catalyst in the kinetics. The results of the model indicate the high influence of variations of small residence times in this process, and the reduction of this effect at high temperatures. Also, the effect of the number of surface sites is shown to be more prominent at low residence times and temperatures. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2228–2234, 2014
Keywords: methane decomposition, carbon catalyst, surface sites, reaction kinetics, numerical modeling

Introduction

Hydrogen is an attractive fuel for the future. The application of this fuel considerably reduces greenhouse gas emissions compared to current methods of producing energy.[1] At present, the reforming of methane is the main method of hydrogen production.[2] The efficiency of this method is rather high,[3] but it has the disadvantage of producing a significant amount of CO_2 gas as a by-product.[4] The alternative method of decomposition of methane has been proposed for hydrogen production, with the benefit of considerably reducing the CO_2 produced.[5] Another advantage of the decomposition method is the production of carbon, which holds 42% of the energy of the input gas[6,7] and can be used in future technologies such as carbon direct fuel cells.[8] An overall comparison shows that the decomposition method is a valuable field of research as a technology for hydrogen production in the future,[7] and it has, therefore, been the subject of many investigations in recent years.

To produce a substantial amount of hydrogen, the decomposition of methane is either performed with a catalyst,[9–11] or at high temperatures commonly obtained from solar energy conversion.[7,12] The catalysts used in this process are classified into two main groups of metals and carbons. The application of transition metal catalysts, such as Ni or Co, in the decomposition of methane for the production of carbon dates back to several decades ago.[13] These catalysts have a high initial activity and considerably decrease the operating temperature. However, they are rapidly deactivated due to the deposition of carbon, which removal results in the production of large amounts of CO_2. Conversely, carbon catalysts, which were originally proposed by Muradov,[14] remain active for longer periods, and also enable the use of the deposited carbon as a marketable by-product instead of its removal from the deactivated catalyst. The use of carbonaceous catalysts also offers other advantages such as durability, availability, and low cost.

Multiple experimental studies have been performed on the decomposition of methane with carbon as the catalyst.[6,10,15–32] In these experiments, the activity and deactivation of several types of carbons and their variations with operating conditions such as temperature and gas velocity have been investigated. To explain the discrepancies observed in the behavior of different types of carbon catalysts their characteristics, that is, textural properties, surface chemistry, and surface morphology, were compared with their activities. The results of these studies suggest that a portion of the sites available on the surface of the catalyst, called the active sites, are more prompt to react with the surrounding gas, and the number of these sites is different in various types of catalysts. It is generally accepted that defects and irregularities on the surface of the catalyst form active sites. Therefore, the number of active sites is a function of the characteristics of the surface of the catalyst. Although methods have been suggested for obtaining a comparative amount of the number of active sites on different type of carbon catalysts,[26,33] a general method has not yet been established to find this value.

While the thermocatalytic decomposition of methane with carbon catalyst has been widely investigated in experimental studies, modeling of this process is very limited. A number of models have been developed for solar reactors with a flow of methane laden with carbon particles.[34–37] The reaction rate in all of these models has been obtained with a simplified rate law, without including the effect of variations in surface sites. A model has also been proposed for fluidized-

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bed reactors by Dunker et al.,[38] where the kinetics is represented by elementary reactions. In this model, the number of surface sites is assumed constant and equal to the surface sites of soot particles for all different types of carbon catalysts, and during the whole experiments.

It can be concluded that two shortcomings are observed in the investigation of the activity of carbon catalysts: the number of surface sites of carbon catalysts has not been quantified yet, and its effect has not been considered in any of the existing models. The aim of this article is to address these two issues by developing a model to estimate the number of surface sites of different types of catalysts, and use it to investigate the effect of this value on the activity of the carbon catalysts in different conditions. Consequently, a stationary fluidized-bed reactor of carbon particles with an input of methane is modeled to calculate the amount of outlet hydrogen, whereas considering the effect of surface sites in the kinetic part of the model. The fluidized bed was chosen as the reactor in this study as it has a high-mass and -heat transfer, and also provides the possibility of a continuous operation for the process by removing the produced carbon. In the first section of this article, the model of the reactor is presented, and the inclusion of the surface sites is explained. In the next section, experimental values available from literature are used to calculate the required constants and to complete the model. The value of the number of active surface sites of different carbon catalysts used in the experiments are then estimated using the model. Finally, the effects of temperature, residence time, and number density of surface sites are investigated on the amount of hydrogen produced in the process.

Model Description

The overall purpose of modeling the reactor for the decomposition of methane in this study is to find the amount of hydrogen in the exhaust stream. The composition of the exhaust mixture from the reactor is determined using the time-dependent continuity equation for each gas species in an isothermal well-stirred reactor as follows[39,40]:

$$\frac{dY_k}{dt}=\frac{1}{\tau}\left(Y_{k,\mathrm{in}}-Y_k\right)+\frac{\dot{\omega}_k \mathrm{MW}_k}{\rho} \qquad k = 1, \ldots, N \tag{1}$$

In this equation, Y_k and $Y_{k,\mathrm{in}}$ are the mass fractions of the kth species at the exit and inlet of the reactor, respectively, τ is the residence time of the gas in the reactor, ρ is the density, and MW_k the molecular weight of the kth species. The variable $\dot{\omega}_k$in Eq. 1 represents the molar production rate of the kth species. This value involves the production rates from the interaction of gas-phase species with each other, and the additional production rate due to the presence of the catalyst particles.

The production rate from the interaction of gas-phase species is calculated with a mechanism of 242 elementary reactions and 75 species previously developed by the authors for the production of hydrogen from thermal decomposition of methane.[39] This mechanism was obtained using several major mechanisms of combustion of light hydrocarbons.

The production rate of gaseous species from the surface of particles is obtained using a mechanism of surface reactions proposed by Dunker et al.,[38] which is presented bellow.

$$\mathrm{C_s{-}H + H \rightleftarrows C_s\bullet + H_2} \tag{R1}$$

$$\mathrm{C_s\bullet + H \rightarrow C_s{-}H} \tag{R2}$$

$$\mathrm{C_s\bullet + C_2H_2 \rightarrow C_s{-}H + H} \tag{R3}$$

$$\mathrm{C_s\bullet + C_2H_6 \rightleftarrows C_s{-}H + C_2H_5} \tag{R4}$$

$$\mathrm{CH_4(+C_s{-}H) \rightleftarrows CH_3 + H(+C_s{-}H)} \tag{R5}$$

$$\mathrm{C_2H_4(+C_s{-}H) \rightleftarrows C_2H_2 + H_2(+C_s{-}H)} \tag{R6}$$

$$\mathrm{C_2H_6(+C_s{-}H) \rightleftarrows CH_3 + CH_3(+C_s{-}H)} \tag{R7}$$

$$\mathrm{C_2H_5(+C_s{-}H) \rightleftarrows C_2H_4 + H(+C_s{-}H)} \tag{R8}$$

In this mechanism, the surface sites on the carbon catalyst are considered to be in the form of carbon radical,$\mathrm{C_s\bullet}$, and carbon atoms saturated with hydrogen, $\mathrm{C_s{-}H}$. The first three reactions and their rate coefficients were directly taken from the surface growth mechanism in the soot formation model of Appel et al.[41] The remaining reactions were added by Dunker et al. to model the decomposition of methane. The rate of reactions R1–R4 is calculated with the following equation[42]:

$$r_i=k_i C_i \frac{f_s \chi_s A_s}{N_A} \qquad i=1,\ldots,4 \tag{2}$$

where $k_i$is the per-site rate coefficient obtained by analogy with gas-phase reactions, A_s is the total surface area of the particles, and N_A is Avogadro's number. Depending on, whether the forward or reverse rate is calculated, C_i and $f_\mathrm{s}\chi_\mathrm{s}$ are the molar concentration of the gaseous species and the number density of the active surface sites in the reactants or products, respectively. The role of the number density of active sites of the catalyst is clearly observed in Eq. 2. This value has been written in the form of a factor f_s multiplied in χ_s, the number density of surface sites on soot particles, which is considered as a base value in this study. f_s can, therefore, be defined as the ratio of number density of active sites of the catalyst to that of soot. This factor was added in this study to the original equation to account for the difference in the number of active sites in various types of carbon, and also to consider its variations during the process. As there is not any experimental or theoretical method to find the number of active surface sites on carbon catalysts, f_s is obtained with experimental data and this model, using a procedure explained in the next section. In soot formation models, Eq. 2 originally includes a factor α, which is the fraction of surface sites available for chemical reactions. This factor reflects the variations of the activity of soot particles in different flames and its change with temperature. α is only meaningful at high temperatures and its value is unity in the temperature range used in the process of interest in this study, and has therefore been omitted from Eq. 2.

It is also noted that, in these calculations, the number density of $\mathrm{C_s{-}H}$ for soot is 2.3×10^{15} $\mathrm{cm^{-2}}$,[42] while the number density of $C_s\bullet$ is calculated with a steady-state assumption for this radical as follows:

$$\chi_{\mathrm{C_s\bullet}}=\frac{k_1[\mathrm{H}]+k_{-4}[\mathrm{C_2H_5}]}{k_{-1}[\mathrm{H_2}]+k_2[\mathrm{H}]+k_3[\mathrm{C_2H_2}]+k_4[\mathrm{C_2H_6}]}\chi_{\mathrm{C_s{-}H}} \tag{3}$$

The forward rate of reactions R5–R8 is obtained from Eq. 4, which was derived using the kinetic theory,[43,44] considering the collision efficiency. The reverse rate of these reactions is calculated using the equilibrium constant.

$$r_i=f_s \gamma_i C_i A_s \sqrt{\frac{k_\mathrm{B} T}{2\pi m_i}} \quad i = 5,\ldots, 8 \tag{4}$$

In this equation, γ_i is the collision efficiency of the ith reaction, m_i is the mass of the reactant, and k_B is the Boltzmann constant. The method applied to find the collision efficiency will be discussed in the following section. It is noted that the derivation of the rate of reaction from kinetic theory and the definition of f_s have lead to the inclusion of this factor in Eq. 4.

The rate of the surface reactions derived from Eqs. 2 and 4 provides the production rate of gaseous species from interaction with the catalyst. The sum of this value and the production rate from the homogeneous phase of the process determines the total production rate that is to be used in Eq. 1.

The dependence of the model on the particle distribution is caused by the variations of the total surface area in Eqs. 2 and 4, due to both physical and chemical phenomena. To account for these changes, the particle dynamics was modeled with the method of moments developed by Frenklach.[45] This method has been widely used in combustion studies for modeling soot formation due to its computational efficiency. The initiative of this model is the application of moments of the particles, defined below, to describe the distribution of particles.

$$M_r=\sum_{i=1}^{\infty} i^r N_i \quad r = 0,\ 1,\dots,5 \tag{5}$$

In this equation, M_r is the rth moment, i is the number of carbon atoms, and N_i the number density of size i particles. The changes in the moment are obtained by considering the combined effect of nucleation, condensation, and surface growth on the carbon catalyst, similar to the soot formation models. The application and derivation of the model of these phenomena can be found in literature.[44,45] In contrary to the soot formation model, coagulation was omitted in this study according to the results of Dunker et al.[38]

The composition of the outlet mixture from the reactor is determined by solving the system of initial value ordinary differential equations (ODE) formed by combining the continuity equations of all the species, Eq. 1, and the differential equations of moment variations with a variable coefficient ODE solver, DVODE.[46]

Results and Discussion

The model described in this article can be used to study the effect of different parameters such as temperature, residence time, and number of surface sites of the catalyst on the amount of hydrogen production. However, the values of the collision efficiency of reactions R5–R8, and f_s should first be specified. The experimental data of Dunker et al.[47] are used for this purpose. In these experiments, methane was decomposed in a fluidized-bed reactor of carbon particles. Experiments (14) were performed in a temperature range of 1080–1260 K and residence time between 4 and 9 s, with three different commercial carbon black catalysts of Black Pearls 120 (BP120), Black Pearls 2000 (BP2000), and Vulcan XC-72 (XC72). The amount of hydrogen production was measured in each case, in different times of the run. Data collected from these experiments show that like other carbon blacks, the mentioned catalysts have a high initial activity at the beginning of the experiments, which decreases with time, until a quasisteady state is reached with a rather constant amount of hydrogen production.

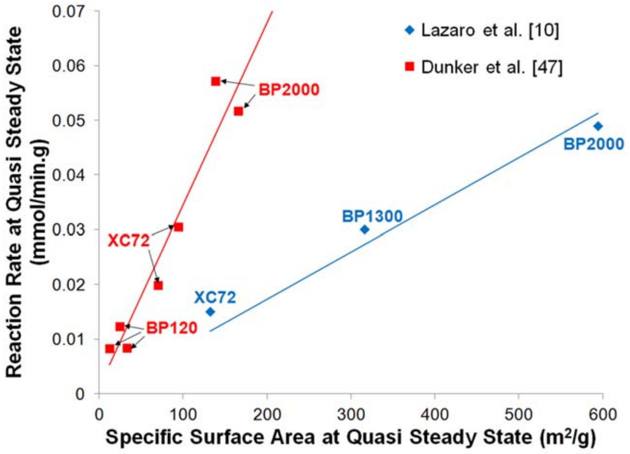

Figure 1. Variations of reaction rate vs. specific surface area at quasisteady-state condition.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The value of collision efficiencies are determined using the data at the quasisteady condition. Experimental studies have shown that the initial activity of catalysts and their specific surface area are not proportional,[6,10,16–19,28] and lead to the conclusion that the number density of active sites of various catalysts differs. However, at the quasisteady conditions, the activity of carbon blacks varies linearly with the specific surface area of the fresh catalyst until it reaches a maximum and then stays constant.[19,21,22] It is noted that the later comparisons were made between the activity of the catalyst at quasisteady state and the surface area of the fresh catalyst, whereas comparing these values at the same condition leads to more valuable conclusions. In this study, experimental data of Lazaro et al.[10] and Dunker et al.[47] were used in Figure 1 to show that the trend of variations of the activity and specific surface area becomes completely linear when both of these values are considered at the quasisteady-state condition. This can be explained by the fact that carbons with higher specific surface areas, such as BP2000, have generally larger fraction of pores, which are rapidly blocked by the deposited carbon, causing a larger decrease in specific surface area relative to catalysts with lower initial surfaces areas.

The linear trend observed in Figure 1 implies that the number density of active sites of different carbon blacks converges to an identical value at the quasisteady-state condition. In this study, this value is considered equivalent to soot. Accordingly, f_s of the carbon catalysts at the quasisteady-state condition is set equal to one.

The ratio of collision efficiencies of reactions R5–R8 and the corresponding gas-phase reactions are assumed equivalent, and the collision efficiencies of these reactions are found to be $9 \pm 1 \times 10^{-11}$, $5 \pm 0.5 \times 10^{-09}$, $1.35 \pm 0.15 \times 10^{-06}$, and 0.41 ± 0.05, respectively. It is noted that applying reaction probabilities in the specified ranges yields in similar amounts of hydrogen. The results of the model with these collision efficiencies, at quasisteady conditions closely follow experimental values as shown in Figure 2.

The factor f_s for each catalyst can now be determined using experimental data at the start of each run. The amount of hydrogen production obtained from the model with f_s equal to one, which implies a number density of surface sites

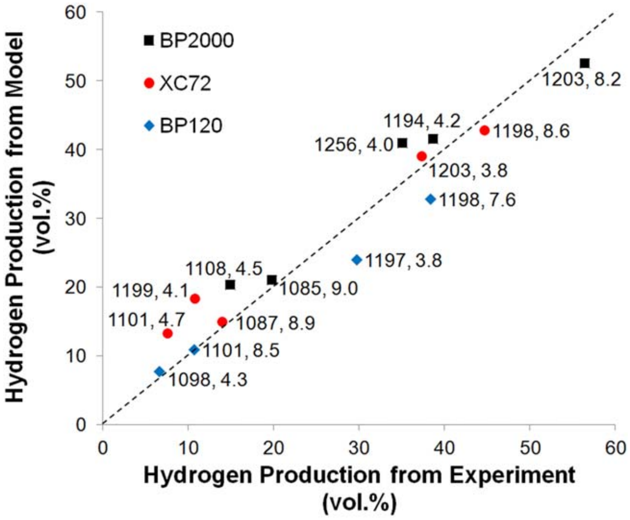

Figure 2. Volumetric percentage of hydrogen production obtained from model compared to experimental values at quasisteady-state conditions.

The values in the labels show the temperature in Kelvin and residence time in seconds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equal to soot particles, is compared with experimental results in Figure 3A. It is observed that using soot properties, the values of hydrogen obtained from the model are significantly lower than experimental values. This can be explained by the fact that carbon catalysts are more active than soot particles and have a higher number of active surface sites, which should be considered in the model. This justifies the use of the factor f_s in the calculation of reaction rates. This factor can be determined by adjusting the results of the model with experimental data for each of the catalysts. This investigation shows that the initial number of active surface sites per unit mass of the catalyst for BP120, XC72, and BP2000 is 7×10^{17}, 1×10^{18}, and 2×10^{19} g^{-1}, respectively. This is in agreement with experimental studies, which show that BP2000 has a higher degree of disorder and more defects than XC72.[26] The results obtained by introducing the values obtained for f_s in the model are presented in Figure 3B, and are in reasonable agreement with experimental data.

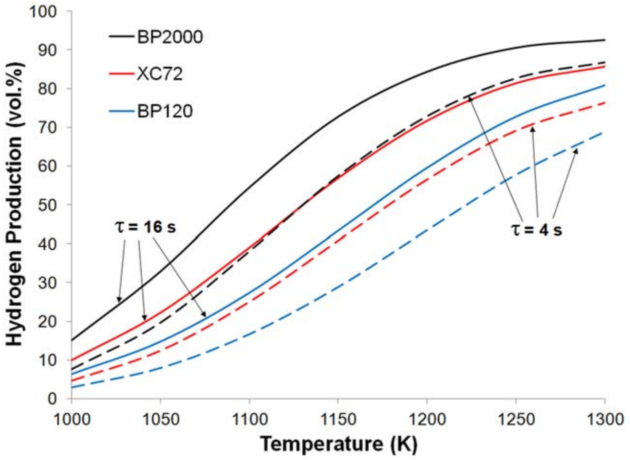

Figure 4. Variations of the initial hydrogen production with temperature, at residence times of 4 (dashed lines), and 16 (solid lines) s for BP120, BP2000, and XC72.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Overall, it can be concluded from Figures 2 and 3B that the values obtained from the model can reasonably predict the amount of hydrogen production.

After determining the collision efficiencies and the factor f_s, the model developed in the previous section was used to find the effect of temperature and residence time on the amount of hydrogen produced from the carbon catalysts BP120, BP2000, and XC72. The results are presented in Figures 4 and 5. It is observed that hydrogen production from all catalysts increase with temperature and residence time, and the trend of variations is similar for all catalysts. The amount of hydrogen produced with the BP2000 at each temperature and residence time is significantly higher than the two other catalysts. This can be explained by the fact that the number density of active sites on BP2000 is around 20 and 30 times higher than that of

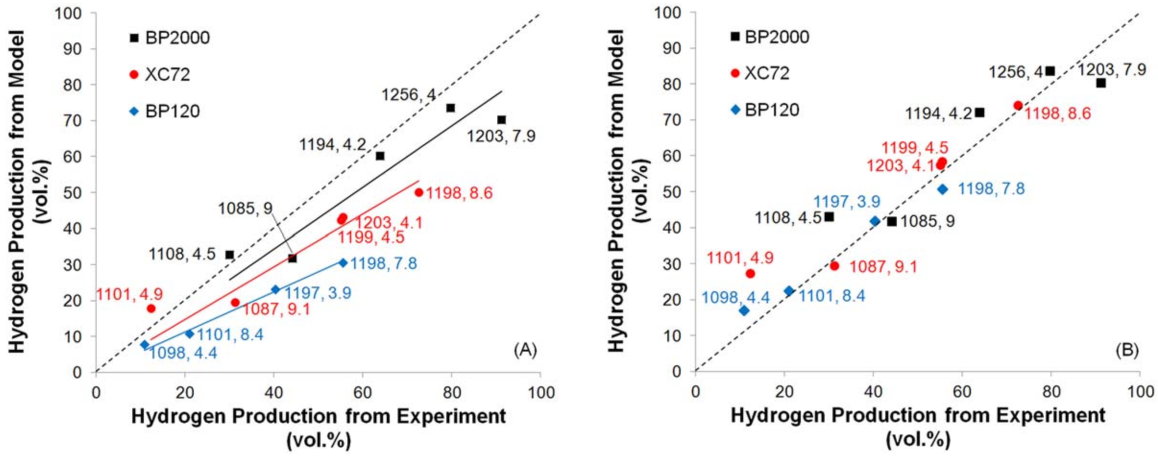

Figure 3. Initial percentage of hydrogen production obtained from experiments compared to model with: (A) number density of surface sites equal to that of soot and (B) adjusted number density of surface sites.

The values in the labels show the temperature in Kelvin and residence time in seconds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

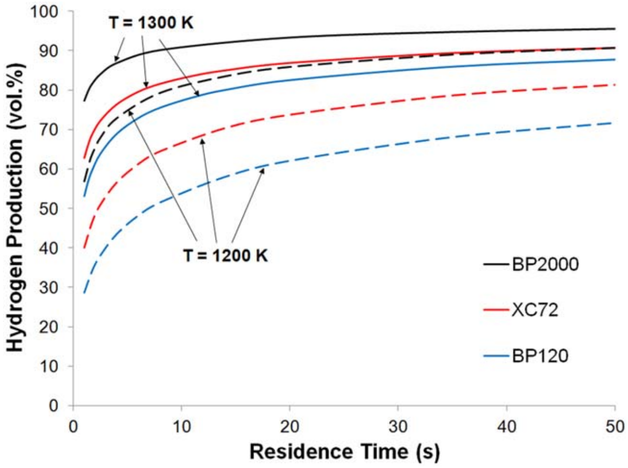

Figure 5. Variations of the initial hydrogen production with residence time at 1200 (dashed lines) and 1300 (solid lines) K for BP120, BP2000, and XC72.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

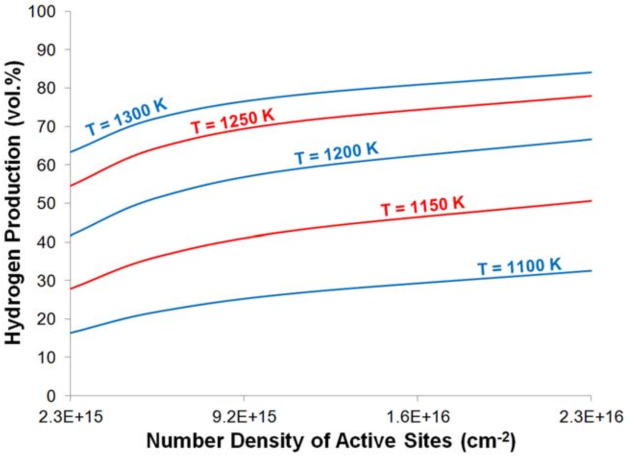

Figure 7. Variations of the initial hydrogen production with the number density of active sites at different temperatures with a residence time of 4 s.

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XC72 and B120, respectively. Figure 4 shows that a small amount of hydrogen is produced at low temperature with all catalysts. As the temperature rises, the difference between the hydrogen production with various catalysts increases until it reaches a maximum between 1150 and 1200 K, and then decreases again.

Figure 5 shows that changing the residence time from 1 to around 10 s significantly affects the amount of hydrogen production, whereas an increase beyond 10 s creates a much smaller effect; for example, for XC72 at 1200 K, hydrogen production is doubled when the residence time is changed from 1 to 50 s; whereas half of this variation is achieved with a residence time of 7 s. It is also observed that as the temperature increases, the effect of residence time is reduced, especially for BP2000. This effect can be explained by considering that the difference between the hydrogen production at a specific residence time and the equilibrium value is much larger at low temperatures due to a slower reaction. The larger difference in this value initiates the higher effect of residence time.

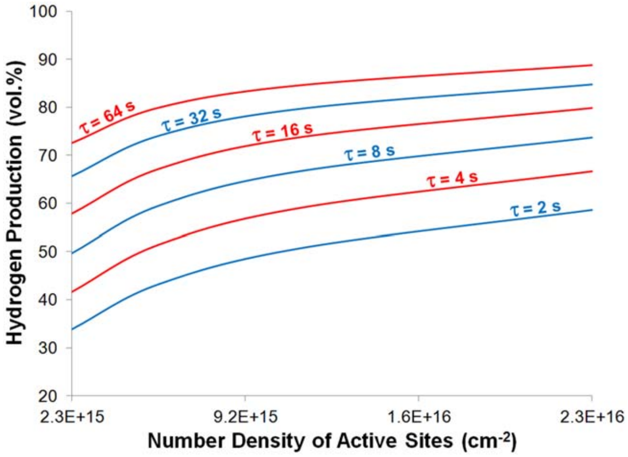

Figure 6. Variations of the initial hydrogen production with the number density of active sites at 1200 K with different residence times.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The model was also used to find the effect of the number density of surface sites on hydrogen production. For this purpose, a specific surface area equal to XC72 was considered, whereas the number density of active sites started with the base value of soot particles and was increased by a factor of up to 10. The variation of hydrogen production with the number density of active sites, and the effect of temperature and residence time on it are shown in Figures 6 and 7, respectively. As expected, hydrogen production at each temperature and residence time increases with the number density of active sites. Figure 6 shows that this increase is more noticeable at lower residence times; at 1200 K, the increase in hydrogen production is more than 70% with a residence time of 2 s, whereas it is only 20% with 64 s. Since the rate of the reaction is lower when the number of surface sites is small, the increase in residence time creates a higher effect on the rate of collision of species with surface sites and, therefore, creates a larger change in the hydrogen production. Figure 7 shows that the variations of hydrogen production due to changes in active sites are higher at low temperatures; with a residence time of 4 s, these variations are around 100 and 30% at 1100 and 1300 K, respectively.

Conclusions

A model was developed for the thermocatalytic decomposition of methane in a fluidized bed of carbon particles that includes the effect of active surface sites. The amount of hydrogen from the process was obtained by combining the production from the interaction of gas-phase species with each other, and the additional production due to the presence of the catalyst particles. The gas-phase kinetics was represented by a reaction mechanism previously developed by the authors,[39] and a mechanism proposed by Dunker et al.[38] was modified to model the surface reactions. The effect of variations of the number of active sites with the type of the catalyst and during the process was included in the model by modifying the equations of the rates of surface reactions. To the best knowledge of the authors, this is the first model to incorporate the effect of the number of active sites on the surface of carbon catalysts in the decomposition of methane. A method was presented to estimate the number density of active sites with the model and experimental data. Accordingly, the initial number of active surface sites per unit mass of three commercial carbon blacks, BP120, XC72, and BP2000 were determined to be 7×10^{17}, 1×10^{18}, and 2×10^{19} g^{-1}, respectively. The model was then used to study the effect of number of surface sites, temperature, and residence time on hydrogen production. The results show that increasing small residence times can lead to a significantly higher amount of hydrogen production, whereas changing large residence times can only cause a slight improvement. However, increasing the temperature reduces the effect of residence time. It was also concluded that the effect of the number of surface sites is higher at low residence times and temperatures.

The results obtained in this article can be used as a guideline to choose between several catalysts considering their characteristics, or to suggest appropriate operating conditions. The model developed can be used to find the optimum operating and design parameters of the process. However, it should be mentioned that a complete optimization can only be performed when other parameters such as economic factors are considered. It is also noted that the results obtained in this study are related to the initial activity of the catalysts. To perform a complete comparison between the different catalysts, the rate of deactivation should be added to the model.

Acknowledgment

The financial support of The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

Notation

A_s = surface area of the particles, m^2
C = molar concentration of gaseous species, mol/m^3
f_s = ratio of number density of active surface sites on catalyst to that of soot
i = number of carbon atoms in a particle
k = per-site rate coefficient of surface reactions, 1/mol s
k_B = Boltzmann constant, 1.3807×10^{-23} m^2 kg/s^2 K
m = mass of reactant, kg
M_r = rth moment, $1/m^3$
MW = molecular weight, kg/mol
N_A = Avogadro's number, 6.022×10^{23} 1/mol
N_i = number density of size i particles, $1/m^3$
r = Reaction rate, mol/m^3 s
Y = mass fraction

Greek letters

γ = collision efficiency
ρ = density, kg/m^3
τ = residence time of the gas in the reactor, s
χ_s = number density of surface sites on soot particles, $1/m^2$
$\dot{\omega}$ = molar production rate, mol/m^3 s

Subscripts

i = number of reaction
in = reactor inlet
k = number of species

Literature Cited

1. Muradov NZ, Veziroglu TN. From hydrocarbon to hydrogen–carbon to hydrogen economy. *Int J Hydrogen Energy*. 2005;30:225–237.
2. Marban G, Valdes-Solis T. Towards the hydrogen economy. *Int J Hydrogen Energy*. 2007;32:1625–1637.
3. Abbas HF, Wan Daud WMA. Hydrogen production by methane decomposition: a review. *Int J Hydrogen Energy*. 2010;35:1160–1190.
4. Dincer I. Green methods for hydrogen production. *Int J Hydrogen Energy*. 2012;37:1954–1971.
5. Muradov N. Thermocatalytic CO_2-free production of hydrogen from hydrocarbon fuels. In: *Proceedings of the 2002 U.S. DOE Hydrogen Program Review*, NREL/CP-610–32405, Golden, CO, 2002.
6. Suelves I, Lazaro MJ, Moliner R, Pinilla JL, Cubero H. Hydrogen production by methane decarbonization: carbonaceous catalysts. *Int J Hydrogen Energy*. 2007;32:3320–3326.
7. Steinberg M. Fossil fuel decarbonization technology for mitigating global warming. *Int J Hydrogen Energy*. 1999;24:771–777.
8. Cao D, Sun Y, Wang G. Direct carbon fuel cell: fundamentals and recent developments. *J Power Sources*. 2007;167:250–257.
9. Muradov N, Chen Z, Smith F. Fossil hydrogen with reduced CO_2 emission: modeling thermocatalytic decomposition of methane in a fluidized bed of carbon particles. *Int J Hydrogen Energy*. 2005;30: 1149–1158.
10. Lazaro MJ, Pinilla JL, Suelves I, Moliner R. Study of the deactivation mechanism of carbon blacks used in methane decomposition. *Int J Hydrogen Energy*. 2008;33:4104–4111.
11. Takenaka S, Shigeta Y, Tanabe E, Otsuka K. Methane decomposition into hydrogen and carbon nanofibers over supported Pd–Ni catalysts. *J Catalysis*. 2003;220:468–477.
12. Rodat S, Abanades S, Flamant G. High-temperature solar methane dissociation in a multitubular cavity-type reactor in the temperature range 1823–2073 K. *Energy Fuels*. 2009;23:2666–2674.
13. Robertson SD. Carbon formation from methane pyrolysis over some transition metal surfaces-I. Nature and properties of the carbons formed. *Carbon*. 1970;8:365–368.
14. Muradov NZ. CO_2-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel. *Energy Fuels*. 1998;12:41–48.
15. Muradov N. Catalysis of methane decomposition over elemental carbon. *Catal Commun*. 2001;2:89–94.
16. Muradov N, Smith F, T-Raissi A. Catalytic activity of carbons for methane decomposition reaction. *Catal Today*. 2005;102–103:225–233.
17. Muradov N. Hydrogen via methane decomposition: an application for decarbonization of fossil fuels. *Int J Hydrogen Energy*. 2001;26: 1165–1175.
18. Kim MH, Lee EK, Jun JH, Kong SJ, Han GY, Lee BK, Lee TJ, Yoon KJ. Hydrogen production by catalytic decomposition of methane over activated carbons: Kinetic study. *Int J Hydrogen Energy*. 2004;29(2):187–193.
19. Lee EK, Lee SY, Han GY, Lee BK, Lee TJ, Jun JH, Yoon KJ. Catalytic decomposition of methane over carbon blacks for CO_2-free hydrogen production. *Carbon*. 2004; 42:2641–2648.
20. Lee KK, Han GY, Yoon KJ, Lee BK. Thermocatalytic hydrogen production from the methane in a fluidized bed with activated carbon catalyst. *Catal Today*. 2004;93–95:81–86.
21. Ryu BH, Lee SY, Lee DH, Han GY, Lee TJ, Yoon KJ. Catalytic characteristics of various reinforcing carbon blacks in decomposition of methane for hydrogen. *Catal Today*. 2007;123:303–309.
22. Lee SY, Ryu BH, Han GY, Lee TJ, Yoon KJ. Catalytic characteristics of specialty carbon blacks in decomposition of methane for hydrogen production. *Carbon*. 2008;46:1978–1986.
23. Serrano DP, Botas JA, Pizarro P, Guil-Lopez R, Gomez G. Ordered mesoporous carbons as highly active catalysts for hydrogen production by CH4 decomposition. *Chem Commun*. 2008;48:6585–6587.
24. Botas JA, Serrano DP, Guil-Lopez R, Pizarro P, Gomez G. Methane catalytic decomposition over ordered mesoporous carbons: A promising route for hydrogen production. *Int J Hydrogen Energy*. 2010;35: 9788–9794.
25. Serrano DP, Botas JA, Guil-Lopez R. H_2 production from methane pyrolysis over commercial carbon catalysts: kinetic and deactivation study. *Int J Hydrogen Energy*. 2009;34:4488–4494.
26. Serrano DP, Botas JA, Fierro JLG, Guil-Lopez R, Pizarro P, Gomez G. Hydrogen production by methane decomposition: origin of the catalytic activity of carbon materials. *Fuel*. 2010;89:1241–1248.
27. Guil-Lopez R, Botas JA, Fierro JLG, Serrano DP. Comparison of metal and carbon catalysts for hydrogen production by methane decomposition. *Appl Catal A*. 2011;396:40–51.
28. Moliner R, Suelves I, Lazaro MJ, Moreno O. Thermocatalytic decomposition of methane over activated carbons: influence of

textural properties and surface chemistry. *Int J Hydrogen Energy*. 2005;30:293–300.

29. Pinilla JL, Suelves I, Lazaro MJ, Moliner R. Kinetic study of the thermal decomposition of methane using carbonaceous catalysts. *Chem Eng J*. 2008;138:301–306.
30. Suelves I, Pinilla JL, Lazaro MJ, Moliner R. Carbonaceous materials as catalysts for decomposition of methane. *Chem Eng J*. 2008;140:432–438.
31. Bai Z, Chen H, Li W, Li B. Hydrogen production by methane decomposition over coal char. *Int J Hydrogen Energy*. 2006;31:899–905.
32. Kameya Y, Hanamura K. Carbon black texture evolution during catalytic methane decomposition. *Carbon*. 2012;50:3503–3512.
33. Lee SY, Kwak JH, Han GY, Lee TJ, Yoon KJ. Characterization of active sites for methane decomposition on carbon black through acetylene chemisorption. *Carbon*. 2008;46:342–348.
34. Patrianakos G, Kostoglou M, Konstandopoulos A. One-dimensional model of solar thermal reactors for the CO-production of hydrogen and carbon black from methane decomposition. *Int J Hydrogen Energy*. 2011;36:189–202.
35. Caliot C, Flamant G, Patrianakos G, Kostoglou M, Konstandopoulos AG. Two-dimensional model of methane thermal decomposition reactors with radiative heat transfer and carbon particle growth. *AIChE J*. 2012;58:2545–2556.
36. Maag G, Lipinski W, Steinfeld A. Particle–gas reacting flow under concentrated solar irradiation. *Int J Heat Mass Transfer*. 2009;52:4997–5004.
37. Ozalp N, Shilapuram V. Step-by-step methodology of developing a solar reactor for emission-free generation of hydrogen. *Int J Hydrogen Energy*. 2010;35:4484–4495.
38. Dunker AM, Ortmann JP. Kinetic modeling of hydrogen production by thermal decomposition of methane. *Int J Hydrogen Energy*. 2006;31:1989–1998.
39. Younessi Sinaki M, Matida EA, Hamdullahpur F. Development of a reaction mechanism for predicting hydrogen production from homogeneous decomposition of methane. *Int J Hydrogen Energy*. 2011;36(4):2936–2944.
40. Younessi-Sinaki M, Matida EA, Hamdullahpur F. Kinetic model of homogeneous thermal decomposition of methane and ethane. *Int J Hydrogen Energy*. 2009;34:3710–3716.
41. Appel J, Bockhorn H, Frenklach M. Kinetic modeling of soot formation with detailed chemistry and physics: laminar premixed flames of C_2 hydrocarbons. *Combust Flame*. 2000;121:122–136.
42. Frenklach M, Wang H. Detailed modeling of soot particle nucleation and growth. *Proc Combust Inst*. 1991;23:1559–1566.
43. Levine IN. *Physical Chemistry*, 6th ed. New York: McGraw-Hill, 2009.
44. Frenklach, M. On surface growth mechanism of soot particles. *Proc Combust Inst*. 1996;26:2285–2293.
45. Frenklach M, Harris SJ. Aerosol dynamics modeling using the method of moments. *J Colloid Interface Sci*. 1987;118(1):252–261.
46. Brown PN, Byrne GD, Hindmarsh AC. VODE, a variable-coefficient ODE solver. *SIAM J Sci. Stat. Comput*. 1989;10:1038–1051.
47. Dunker AM, Kumar S, Mulawa PA. Production of hydrogen by thermal decomposition of methane in a fluidized-bed reactor—Effects of catalyst, temperature, and residence time. *Int J Hydrogen Energy*. 2006;31:473–484.

Manuscript received Jun 21, 2013, and revision received Dec. 21, 2013.