

POTASSIUM CATALYZED STEAM GASIFICATION OF COAL CHAR IN A PRESSURIZED STREAM OF $\text{H}_2\text{O}-\text{H}_2-\text{CO}$ MIXTURE GAS

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Activated carbon produced from lignite char was impregnated with potassium carbonate and gasified with steam in an $\text{H}_2\text{O}-\text{H}_2-\text{CO}$ mixture gas at total pressure of 1.5 MPa and in the range of temperatures from 973 to 1073 K.

The gasification rate changed with the progress of carbon conversion and showed a maximum value at a carbon conversion around 0.3–0.4. The ratio of the gasification rate at any conversion to the initial rate could be correlated with the extent of carbon conversion by a relation which took into account the structural change of pores constructed in char filled with catalyst. The initial rate of gasification could be represented by a Langmuir-Hinshelwood type equation of single site mechanism including adsorption terms of H_2O and H_2 . The rate constant was found to be roughly proportional to the atomic ratio of potassium to carbon. The apparent activation energy was 97.8 kJ/mol, independently of the potassium content and carbon conversion.

Introduction

Application of solid catalyst to accelerate coal char gasification with steam has attracted much interest as one of the most economical methods to convert fossil solid fuel into a potential chemical raw material or fluid fuel. A number of investigations have been attempted on the enhancement of reactivity of coal char using many kinds of catalysts. Several works have shown that potassium carbonate promotes the steam gasification of coal char most remarkably,^{5,7,9–11,15–18,21} and accelerates the methane formation reaction under pressurized gasification conditions.^{2,15,20} However, there has been speculation about the kinetic mechanism of potassium-catalyzed steam gasification of coal char at elevated pressure. It is requisite to establish a rational rate expression helpful for prediction of the amount of methane formation by steam gasification of coal char with potassium catalyst under pressure.

The purpose of the present study is to obtain gasification data of coal char impregnated with potassium carbonate in a pressurized atmosphere of $\text{H}_2\text{O}-\text{H}_2-\text{CO}$ mixture gas. The gasification rates are examined by varying the partial pressures of gaseous species and the amount of catalyst loaded on char. It will be demonstrated that the variation of gasification

rate with the progress of carbon conversion is described by taking into account the change of pore surface constructed in char impregnated with catalyst. The effect of partial pressure of species on the gasification rate will be investigated on the basis of a Langmuir-Hinshelwood mechanism including the effect of adsorption of reactant gas on the active sites of pore surface in the char.

1. Experimentals

1.1 Materials

Sample materials used in this work were prepared by the same procedures as described in the previous paper.¹³ Activated carbon produced from lignite char (Takeda C-830) of 0.5–1.0 mm size, treated with warm hydrochloric acid to remove ash contained in the sample, was impregnated with special-grade potassium carbonate. Three kinds of samples were prepared, having potassium contents of 0.0133, 0.0627, and 0.109 kg K/kg fixed carbon respectively. The details of sample materials are shown elsewhere.¹³

1.2 Experimental apparatus and procedures

A high-pressure differential-flow packed-bed reactor was used, details of which are described elsewhere.¹³

A weighed amount of sample (0.5–2 grams) was charged in the reactor tube, being sandwiched between quartz wool, at the center of a packed bed of alumina beads. The sample was heated in a stream of Ar gas to a prescribed reaction temperature. Then it

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was contacted with a stream of reactant gases. Steam was prepared by evaporating water supplied to the electrically heated steam generator by a high-pressure micropump. H_2 gas was supplied to the reactor as required, being mixed with steam through the heated pipeline. CO gas was fed to the reactor separately from the others through an unheated pipeline to avoid the water gas-shift reaction with steam and hydrogenation occurring on the metal surface of the reactor. Since the inner wall of the reactor tube is covered with an alumina tube, it was confirmed that any reaction could be neglected in the blank test.

The partial pressure of each reactant gas was adjusted by controlling the respective feed rates of H_2O , H_2 , CO gases and Ar gas as balance. The flow rate of the reactant gas in the reactor was maintained at levels where the gas-film resistance around the external surface of particles could be neglected and the conditions of the differential-flow reactor could be satisfied. The effect of intraparticle diffusion resistance on the gasification rate was negligible in the range of particle size used.

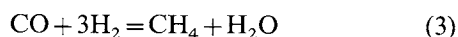
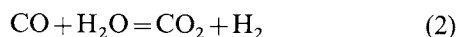
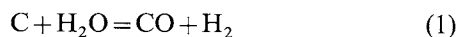
Total pressure was controlled by a back-pressure regulator at 1.5 MPa and reaction temperature was varied in the range of 973 to 1073 K. The composition of product gas was analyzed by gas chromatography after drying by bubbling through sulfuric acid. The flow rate of the dried product gas was measured by a gas meter.

After the desired carbon conversion was reached, the run was stopped and the sample, allowed to cool in Ar gas before being removed from the reactor, was subjected to pore structural analyses. The specific surface area was determined using the Dolimore-Heal equation with N_2 adsorption. The pore volume was measured by a mercury porosimeter capable of registering a minimum pore radius of 5 nm.

2. Results and Analyses

2.1 Simultaneous proceeding reactions

In the steam gasification of coal char, several reactions occur simultaneously. Thus,



When the sample is contacted with a reactant gas containing H_2O , H_2 and CO in a differential-flow reactor, reactions (1), (2), (3), and (5) are considered to occur. Among these reactions, the hydrogenation of carbon represented by Eq. (5) may be neglected in

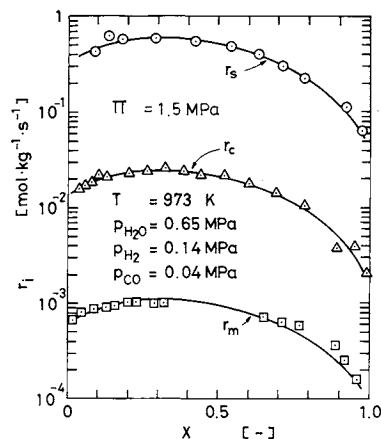


Fig. 1. Variation of each reaction rate with progress of carbon conversion.

relation to the others.¹³⁾ Under differential-flow reactor conditions, the individual rates of reactions (2) and (3) are defined, respectively, as

$$r_s = \frac{1}{W} (F_{CO_2} - F_{CO_2}^0) \quad (6)$$

$$r_m = \frac{1}{W} (F_{CH_4} - F_{CH_4}^0) \quad (7)$$

The rate of steam gasification r_c is defined as follows. The extent of carbon conversion X can be defined as

$$X = \frac{\text{grams of fixed carbon gasified}}{\text{grams of original fixed carbon}} \quad (8)$$

and is given by

$$X = \int_0^t \sum_i (F_i - F_i^0) dt / (W/M) \quad (9)$$

where $i = CO, CO_2, CH_4$.

Thus, r_c is given by

$$r_c = \frac{1}{M} \frac{dX}{dt} = \frac{1}{W} \cdot \sum_i (F_i - F_i^0) \quad (10)$$

Figure 1 illustrates the variation of each reaction rate with the progress of carbon conversion. Under the conditions shown in the figure, CO in the inlet stream was rapidly converted into CO_2 by the shift reaction (2). The rate of the steam gasification (1) follows that of the shift reaction, and the methanation reaction is slowest among them. Each reaction rate takes the maximum value at a carbon conversion around 0.3–0.4. Here, the rate analysis for steam gasification as main reaction shall be conducted. The two other reactions, the shift and methanation, is treated in another paper.

2.2 Overall rate expression of carbon gasification

The rate of steam gasification will be given as the time derivative of carbon conversion. Taking the ratio of the gasification rate at any extent of carbon

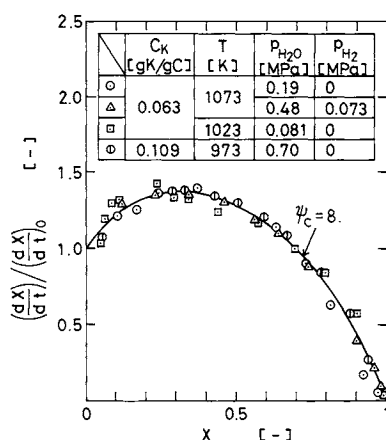


Fig. 2. Variation of gasification rate with carbon conversion under different conditions.

Table 1. Variation of physical properties of sample with progress of carbon conversion

X [—]	a [m ² ·g ⁻¹]	a^* [m ² ·g ⁻¹]	\bar{r}_p [nm]	V_g [cm ³ ·g ⁻¹]	ρ_b [g·cm ⁻³]	ε [—]
0	467	467	2.46	0.301	1.25	0.377
0.22	566	468	2.14	0.336	1.21	0.405
0.41	608	411	1.88	0.346	1.20	0.415
0.57	500	275	1.94	0.282	1.31	0.369

* Represented on the basis of initial char weight.

conversion to the initial rate, several series of data obtained under various conditions are shown in Fig. 2. The initial rate, $(dX/dt)_0$, was evaluated by extrapolating conversion rate plotted against each extent of conversion to $X=0$. As is obvious from the figure, all the gasification rate data behave in a nearly identical fashion, independently of gasification conditions in the range presently investigated. Also, the mode of variation in the catalyzed gasification does not depend on the catalyst content in the range of 0.019 to 0.036 K/C atomic ratio. The gasification rate takes a peak around $X=0.3-0.4$.

Verra *et al.*¹⁸⁾ also reported that in the steam gasification of sub-bituminous coal impregnated with K_2CO_3 in the range 2.5–10 wt% the gasification rate varies with the progress of carbon conversion. However, the mode of variation is different depending on potassium content.

Variation of physical properties of partly converted sample observed on the basis of char weight is shown in Table 1. The specific surface area seems to take a maximum value. Correspondingly, the void fraction takes a maximum value and the char density takes a minimum value. However, the specific surface area represented on the basis of initial char weight decreases monotonously with the progress of carbon conversion, which does not correspond to the variation of gasification rate. The values of the specific

surface area are about one-half those of a sample without catalyst used in uncatalyzed gasification.³⁾ It may be considered that the micropore constructed in sample is filled with particles of potassium catalyst.

We assume that the gasification rate changes in proportion to the pore surface area filled with catalyst per unit volume of char and that the pores within char consist of randomly overlapping cylindrical pores with arbitrary radii according to the model of Bhatia and Perlmutter.¹⁾ The correlation between surface area and extent of carbon conversion can be derived on the basis of the above assumptions. Consequently, the gasification rate can be expressed as follows.

$$dX/dt = (dX/dt)_0(1-X)\sqrt{1-\psi_c \ln(1-X)} \quad (11)$$

where the parameter ψ_c is given by

$$\psi_c = 4(1-\varepsilon_0)/r_{c0}S_{c0} \quad (12)$$

and S_{c0} , r_{c0} , ε_0 are pore surface area coated by catalyst, pore radius and porosity of catalyst loaded-sample at initial state, respectively.

Evaluating dX/dt from rate data and plotting $(dX/dt)^2/(1-X)^2$ against $\ln(1-X)$, a linear relation was obtained. The combination of the intercept and the slope of straight line yielded the value of ψ_c , which was determined to be roughly the same value, 8.0, for all of the experimental data. This value of ψ_c is greater than $\psi_c=2$ obtained in uncatalyzed gasification.⁴⁾ The increase in ψ_c is attributed mainly to the decrease in S_{c0} resulting from the impregnation of catalyst. However, this is still speculative since the surface area effective for reaction cannot be evaluated from the observed BET surface area. The predicted curve was in good agreement with the data, as shown in Fig. 2.

2.3 The rate expression of initial gasification

2.3.1 Effect of partial pressure of species on the initial rate In Fig. 3, the effect of H_2O partial pressure on the initial rate, $(dX/dt)_0$, is shown under conditions where neither H_2 nor CO is contained in the inlet reactant gas. Although $(dX/dt)_0$ increases with the increase in H_2O partial pressure p_{H_2O} , it is suggested from this result that the adsorption of H_2O participates in the gasification process.

Figure 4 shows the gasification rate obtained in the stream of the H_2O-H_2 mixture gas. When p_{H_2O} is kept constant, $(dX/dt)_0$ remarkably decreases with the increase in p_{H_2} . These results imply that the gasification is inhibited by the product hydrogen.

When CO gas is mixed into H_2O , the water gas-shift reaction progresses rapidly and the gasification rate decreases since p_{H_2O} decreases and p_{H_2} increases. Thus, the initial rate under the inlet gas conditions was evaluated by using as little sample as possible and extrapolating $(dX/dt)_0$ to $W=0$. In Table 2, $(dX/dt)_0$ for the H_2O-CO system so obtained is compared with that for the H_2O system. Both values are nearly the

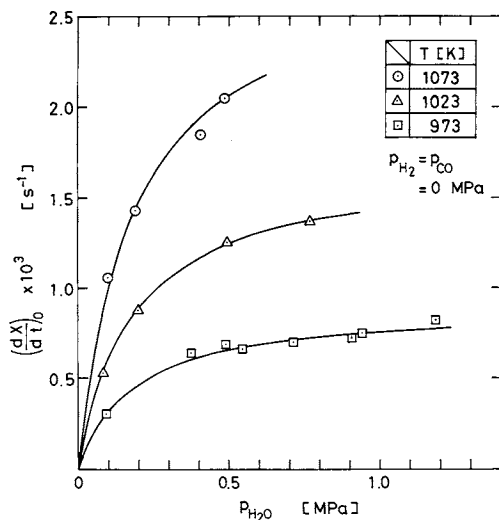


Fig. 3. Effect of steam partial pressure on gasification rate.

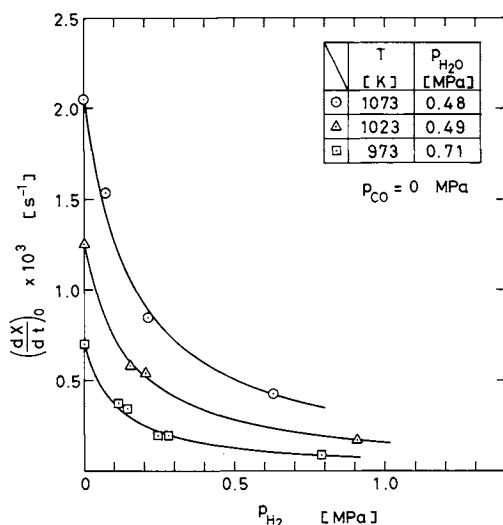


Fig. 4. Effect of hydrogen partial pressure on gasification rate.

Table 2. Comparison of initial gasification rate between H_2O and H_2O-CO systems

T [K]	H_2O system		H_2O-CO system*	
	p_{H_2O} [MPa]	$(dX/dt)_0$ [s ⁻¹]	p_{CO} [MPa]	$(dX/dt)_0$ [s ⁻¹]
973	0.69	7.0×10^{-4}	0.11	6.7×10^{-4}
	0.94	7.5×10^{-4}	0.25	7.6×10^{-4}

* p_{H_2O} is equal to that in H_2O system.

same and the effect of CO on the rate is negligible in the present data.

Let us derive the expression of initial rate. If single-site adsorption of H_2O and H_2 occurs on the pore surface covered by catalyst, the following Langmuir-Hinshelwood type equation can be described similarly as proposed for uncatalyzed gasification in the H_2O-

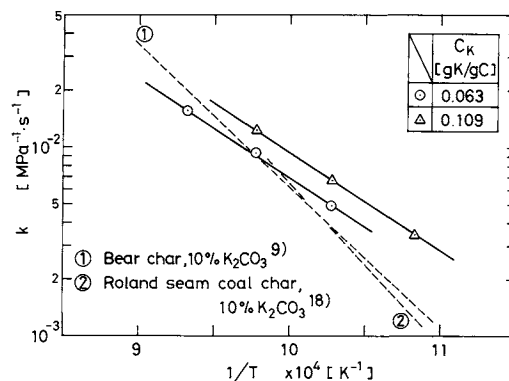


Fig. 5. Arrhenius plot of rate constant k .

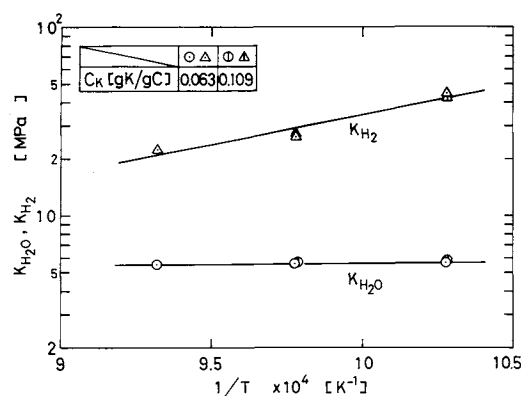


Fig. 6. Temperature dependency of adsorption equilibrium constants for H_2O and H_2 .

H_2 system.^{8,19)}

$$\left(\frac{dX}{dt}\right)_0 = \frac{k p_{H_2O}}{1 + K_{H_2O} p_{H_2O} + K_{H_2} p_{H_2}} \quad (13)$$

When H_2 is not contained in the reactant gas, Eq. (13) may be rewritten as

$$p_{H_2O} \left(\frac{dX}{dt}\right)_0 = \frac{1}{k} + \frac{K_{H_2O}}{k} p_{H_2O} \quad (14)$$

Also, when p_{H_2O} is kept constant, Eq. (13) is rearranged and rewritten as

$$\left(\frac{dX}{dt}\right)_0^{-1} = \frac{(1 + K_{H_2O} p_{H_2O})}{k p_{H_2O}} + \frac{K_{H_2}}{k p_{H_2O}} p_{H_2} \quad (15)$$

The data shown in Fig. 3 were plotted on the basis of Eq. (14), and those shown in Fig. 4 were plotted on the basis of Eq. (15). In both cases, excellent linear relations were obtained. The combination of slope and intercept of each straight line gives the rate constant k and adsorption equilibrium constants K_{H_2O} and K_{H_2} at each temperature.

2.3.2 Temperature dependency of kinetic parameters The Arrhenius type plot of k vs. reciprocal of temperature is shown in Fig. 5. K_{H_2O} and K_{H_2} are plotted against $1/T$ in Fig. 6. Values of K_{H_2O} evaluated respectively by the slope of Eq. (14) and by the intercept of Eq. (15) agreed very well with each

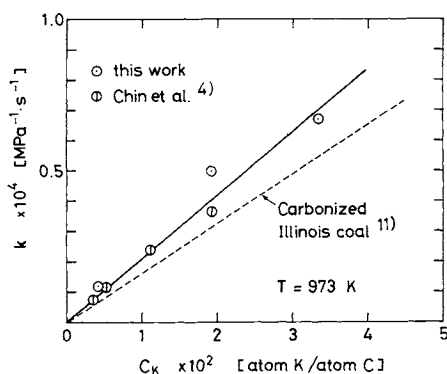


Fig. 7. Dependency of rate constant k on catalyst content.

other.

Since the magnitude of K_{H_2O} is rather small, $(dX/dt)_0$ may be approximated by a first-order rate equation as obtained by Chin *et al.*³⁾ at atmospheric pressure. On the other hand, when H_2 is coexistent with H_2O , Eq. (15) may be reduced to the relation obtained by Mims *et al.*,¹¹⁾ which is proportional to p_{H_2O} and inversely proportional to p_{H_2} .

The temperature dependency of the rate constant does not change with catalyst content, as shown by the pair of parallel lines in Fig. 5. Thus, the apparent activation energy of the rate constant yields 99.6 kJ/mol, independently of catalyst content. This value is not much different from the 117 kJ/mol obtained in uncatalyzed gasification, as estimated from the data by Chin *et al.*³⁾

Kayambe *et al.*⁹⁾ and Verra *et al.*¹⁸⁾ measured the rate of steam gasification of potassium loaded-coal chars at atmospheric pressure. The rate constant could be evaluated from their data by assuming first order with respect to p_{H_2O} . The results are shown in Fig. 5 for comparison with the present results. The magnitudes of the rate constants are not much different from each other. The apparent activation energy of the first-order rate constant is in the range 140–160 kJ/mol and is greater than that of the present data.

Two adsorption equilibrium constants K_{H_2O} and K_{H_2} are not affected by the content of catalyst as shown in Fig. 6. The heats of adsorption equilibrium were evaluated to be 2.64 and 61.1 kJ/mol for H_2O and H_2 , respectively.

2.3.3 Effect of catalyst content and correlations of kinetic parameters Figure 7 shows the effect on the rate constant k of the catalyst content, which is represented by atoms of K per unit atom of fixed carbon. In Fig. 7, the results obtained at atmospheric pressure by Chin *et al.*⁴⁾ are also shown. Since the gasification rate without catalyst is very small, the rate constant is roughly proportional to the catalyst content in this range.

Mims *et al.*¹¹⁾ also found in their atmospheric

experiments that $(dX/dt)_0$ is proportional to the potassium content. The rate constant is evaluated from their data by assuming the same values for K_{H_2O} and K_{H_2} as those of the present system, and results are shown in Fig. 7. Their data with carbonized Illinois coal are very close to the present results.

Vadovic *et al.*¹⁷⁾ carried out the steam gasification of Illinois 6 coal impregnated with K_2CO_3 of 10 and 20 wt%. They obtained by regression analysis a Langmuir-Hinshelwood type rate expression which accounts for the behavior of their data showing that the gasification rate decreases with the increase in H_2O and H_2 partial pressures but, in contrast to the present results, is independent of total pressure. They reported that the pressure-independent rate constant is roughly proportional to potassium content and its activation energy is 125 kJ/mol.

As a result, the kinetic parameters in Eq. (13) can be correlated to temperature and catalyst content by the following equations.

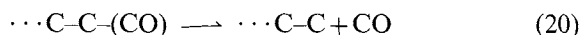
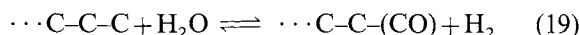
$$k = 3.78 \times 10^4 C_K \exp(-99.6/RT) \quad (16)$$

$$K_{H_2O} = 4.06 \exp(2.64/RT) \quad (17)$$

$$K_{H_2} = 2.33 \times 10^{-2} \exp(61.1/RT) \quad (18)$$

3. Discussion

The reaction kinetics of coal char in a stream of multicomponent gasifying agents has been treated by taking into account the adsorption-surface reaction mechanism on the pore of the solid. The uncatalyzed gasification of carbon with steam has been proposed to occur through the following steps:



Where (C) is carbon atom associated with an active site and (CO) is the oxidized form of the active site. From this simple surface oxide mechanism, a Langmuir-Hinshelwood type rate expression which is equivalent in form to Eq. (13) can be derived.^{8,19)}

Freriks *et al.*⁵⁾ have suggested that the active species in the potassium-catalyzed gasification of carbon with steam is a potassium-containing surface oxide complex. Mims *et al.*¹¹⁾ have shown that the oxygen exchange is catalyzed by the potassium catalyst and occurs at the same sites as shown by Eqs. (19) and (20) in the case of uncatalyzed gasification. Also, product inhibition of gasification occurs through reversal of the oxygen exchange of actual site attacked by hydrogen. When the same rate expression can be described for both catalyzed and uncatalyzed gasification, Eq. (13) can be derived. Equation (13) implies that the potassium-catalyzed gasification of carbon with steam occurs according to a mechanism similar to that of uncatalyzed gasification. The active sites

may be generated as the potassium becomes associated with carbon. Upon decomposition of the surface oxide, a new site may be regenerated together with another neighboring unreacted carbon. The increase in catalyst content may increase the total number of active sites as confirmed experimentally.

On the other hand, the variation of gasification rate could be described by Eq. (11) on the basis of a random-pore model, which accounts for the structure change owing to cylindrical pore radii overlapping with the progress of the reaction. It may be considered that the dispersion state of potassium is uniform and that its contact proportion on the pore surface does not change during gasification. This view may be supported by the result that the apparent activation energy is not affected by either catalyst content or extent of carbon conversion.

Conclusions

Measurements of steam gasification rate of activated carbon impregnated with potassium carbonate were conducted in a pressurized stream of H_2O-H_2-CO mixture gas. The gasification rate could be correlated with carbon conversion by Eq. (11), which was derived by taking into account the structural change of catalyst-loaded pore surface. The ratio of gasification rate at any carbon conversion to the initial rate was independent of gasification conditions except for the carbon conversion. The initial rate was expressed by Eq. (13) on the basis of a Langmuir-Hinshelwood mechanism. The rate constant is roughly proportional to the atoms of potassium per unit atom of fixed carbon, and its apparent activation energy is 99.6 kJ/mol, independently of potassium content. The adsorption equilibrium constants of steam and hydrogen could be correlated with temperature, and their heats of adsorption were 2.64 and 61.1 kJ/mol, respectively. Consequently, the kinetic parameters could be correlated by Eqs. (16)–(18).

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Nomenclature

a	= specific surface area of sample	$[m^2 \cdot g^{-1}]$
C_K	= atoms of potassium per atom of fixed carbon	[—]
E	= apparent activation energy	$[kJ \cdot mol^{-1}]$
F_i	= molar flow rate of gaseous species i at the reactor exit	$[mol \cdot s^{-1}]$
F_i^o	= molar flow rate of gaseous species i at the reactor inlet	$[mol \cdot s^{-1}]$

K_i	= adsorption equilibrium constant for gaseous species i	$[MPa^{-1}]$
k	= gasification rate constant in Eq. (13)	$[MPa^{-1} \cdot s^{-1}]$
M	= atomic weight of carbon	$[kg \cdot mol^{-1}]$
p_i	= partial pressure of gaseous species i	$[MPa]$
R	= universal gas constant	$[kJ \cdot mol^{-1} \cdot K^{-1}]$
r_c	= gasification rate of fixed carbon per unit fixed carbon	$[mol \cdot kg^{-1} \cdot s^{-1}]$
r_m	= rate of methane formation per unit fixed carbon	$[mol \cdot kg^{-1} \cdot s^{-1}]$
\bar{r}_p	= mean radius of pores constructed in sample	$[nm]$
r_s	= rate of water gas-shift reaction per unit fixed carbon	$[mol \cdot kg^{-1} \cdot s^{-1}]$
T	= absolute temperature	$[K]$
t	= reaction time	$[s]$
V_g	= specific volume of void constructed in sample	$[m^3 \cdot kg^{-1}]$
W	= mass of fixed carbon initially contained in sample	$[kg]$
X	= fractional conversion of fixed carbon	[—]
ε	= porosity of solid sample	[—]
ψ_c	= parameter with respect to pore surface properties of solid sample impregnated with catalyst	[—]
P	= total pressure	$[MPa]$

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