Ethylene Selectivity Variation in Acetylene Hydrogenation Reactor with the Hydrogen/Acetylene Ratio at the Reactor Inlet

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Abstract−Variation in the selectivity of ethylene produced by acetylene hydrogenation in an integral reactor was analyzed as a function of the hydrogen/acetylene ratio in the reaction stream at the reactor inlet. The analyses were made for two sample catalysts, which showed different dependence of the ethylene selectivity on the reactant composition. Even a small mismatch between the hydrogen/acetylene ratio at the reactor inlet and the ratio for converted reactants caused a large change in the ethylene selectivity along the reactor position, particularly when the conversion was high. The results of this study indicate two important factors to be considered in the design and operation of acetylene hydrogenation process: the hydrogen/acetylene ratio in the reactor inlet should be controlled close to the ratio for converted reactants; and catalysts showing high ethylene selectivity over a wide range of the hydrogen/acetylene ratio are required for the design of a highly selective hydrogenation process.

Key words: Acetylene Hydrogenation, Pd Catalyst, Ethylene Selectivity, Acetylene Conversion, Integral Reactor, Reactant Ratio

INTRODUCTION

Acetylene included at low levels, 1-2%, in the ethylene stream of a naphtha cracker unit must be removed from the stream such that the latter can be used as a feed for the next polymerization unit. A common method used for acetylene removal is to convert acetylene to ethylene by selective hydrogenation, for which supported Pd catalysts are used [Lam and Llyod, 1972; Cider and Schoon, 1991]. Because ethylene, which is excessively present in the stream, is also hydrogenated to lower-priced ethane in the process, it is important that the production of ethane is minimized while acetylene is converted at maximum rates. In other words, the selectivity of ethylene production should be maximized for an economical operation of the process.

Industrial processes of acetylene hydrogenation use integral reactors to obtain high conversions, and therefore the reactant concentration changes along the axial position of the reactor even when the feed composition is fixed. For example, the ratio of hydrogen and acetylene partial pressures usually changes in the reactor because the ratio of the reactants consumed by the reaction is not always the same as the ratio in the feed.

Such a change in the reactant composition affects the acetylene conversion and the ethylene selectivity obtained in the process. Particularly, the ethylene selectivity is significantly affected by the hydrogen/acetylene ratio [Battiston et al., 1982], and the characteristic relation between the selectivity and the reactant ratio is determined by catalyst used in the process. In this respect, many studies have been made to develop new catalysts that show high ethylene se-

lectivity over a wide range of the hydrogen/acetylene ratio [Leviness et al., 1984; Lee, 1990; Park and Price, 1991; Shin et al., 1998, 2000].

In this study, we have analyzed the reactor for acetylene hydrogenation to obtain characteristic changes in the hydrogen/acetylene ratio and the ethylene selectivity in the reaction stream, and compared the results for two sample catalysts showing different dependence of the ethylene selectivity on the reactant composition.

REACTOR ANALYSIS

1. Variation in the Reactant Composition

Main reactions involved in acetylene hydrogenation are as follows.

$$C_2H_2 + H_2 \rightarrow C_2H_4 \tag{1}$$

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{2}$$

The ethylene selectivity, S, is defined as moles of ethylene produced per mole of converted acetylene. The differential hydrogen/acetylene ratio for converted reactants, $R_{diff}(=dP_{H_2}/dP_{C_2H_2})$, is related to S as follows.

$$R_{diff} = 2 - S \tag{3}$$

Since S cannot exceed 1 and can be a negative value, R_{diff} is any value over 1. For example, when S is 1, only step (1) proceeds between the above two reaction steps and consequently one mole of hydrogen is consumed per mole of converted acetylene, i.e., $R_{diff}=1$. When S is 0, acetylene is completely hydrogenated to ethane by sequential reactions through steps (1) and (2), and consequently two moles of hydrogen are consumed per mole of converted acetylene, i.e., $R_{diff}=2$. When S is negative, which occurs when ethylene excessively included in the feed is converted to ethane by step (2),

more than two moles of hydrogen are consumed per mole of converted acetylene, i.e., $R_{diff} > 2$.

Hydrogen partial pressure, P_{H_2}, changes as acetylene is converted in the reactor.

$$P_{H_2} = P_{H_2}^0 + \int_{P_{H_2}^0}^{P_{H_2}} dP_{H_2} = P_{H_2}^0 + \int_{P_{C_2H_2}^0}^{P_{C_2H_2}} R_{diff} dP_{C_2H_2} = P_{H_2}^0 - P_{C_2H_2}^0 \int_0^x (2-S)dx \quad (4)$$

Accordingly, the $P_{H_2}/P_{C_2H_2}$ ratio, R, is given by Eq. (5) as a function of the acetylene conversion, x.

$$R = \frac{P_{H_2}}{P_{C_2H_2}} = \frac{P_{H_2}^0 - P_{C_2H_2}^0 \int_0^x (2-S)dx}{P_{C_2H_2}^0 (1-x)} = \frac{1}{1-x}[R^0 - \int_0^x (2-S)dx] \quad (5)$$

2. Relation Between the Selectivity and the Reactant Composition

The solution of Eq. (5) is not easy because the ethylene selectivity, S, included in the integral is dependent on the hydrogen/acetylene ratio, R. In other words, we need an expression of the selectivity as a function of the reactant ratio to solve Eq. (5). In this study, we have obtained the following general expression for S as a function of R, Eq. (6), by using a steady-state approximation for the rates of individual reactions involved in acetylene hydrogenation, which are described in Fig. 1. Details of the derivation are given in Appendix I.

$$S = A - \frac{B}{C + D \times R + \sqrt{E + F \times R + G \times R^2}} \quad (6)$$

Coefficients A-G are intrinsically determined by process conditions such as temperature, pressure, and catalyst used in the reaction. In this study, we have estimated the coefficients for two sample catalysts: a commercial Ni-promoted catalyst (Catalyst A) and an Si-promoted catalyst prepared in this laboratory (Catalyst B). We measured the ethylene selectivity at different hydrogen/acetylene ratios using the sample catalysts under the identical reaction conditions, as described in Appendix II, and then estimated coefficients A-G by fitting Eq. (6) to the experimental data.

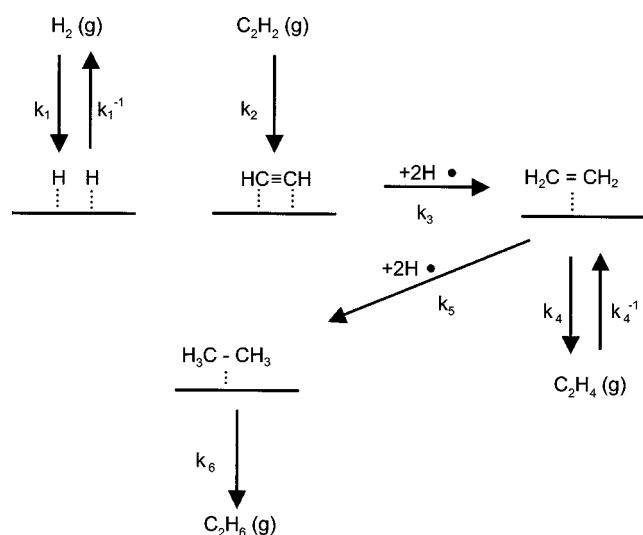Table 1 lists the coefficients estimated by the data fitting for two

Fig. 1. Mechanism of acetylene hydrogenation.

Table 1. Estimated coefficients of Eq. (6)

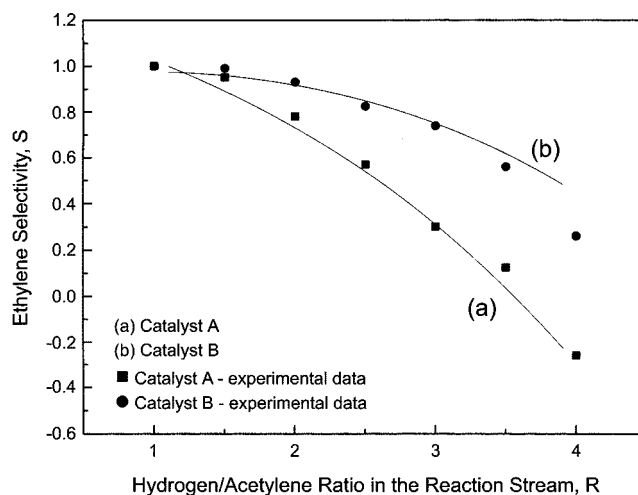| Coefficient	Catalyst A (Commercial catalyst)	Catalyst B (Si-modified catalyst)
A	19.1	30.1
B	15.1	12.9
C	−0.141	−0.472
D	0.0504	0.0539
E	0.969	0.834
F	−0.114	−0.0966
G	1.13×10^{-11}	1.78×10^{-3}

Fig. 2. Correlation curves between ethylene selectivity, S, and the reactant ratio, R, for sample catalysts together with experimental data.

sample catalysts. Fig. 2 also shows the correlation curves between the selectivity, S, and the reactant ratio, R, together with the measured experimental data. The selectivity is almost the same, near unity, for two catalysts when R is close to 1.0, but S decreases as R increases. The extent of the selectivity drop is more significant with Catalyst A than with Catalyst B. That is, the selectivity remains as high as about 0.5 even when R is 4.0 for Catalyst A but drops to negative values at R values beyond 3.5 for Catalyst B.

RESULTS AND DISCUSSION

1. Constant Selectivity

For an initial discussion of the reactor analysis, we have calculated R values for different conversions, x, using Eq. (5) assuming that S is constant throughout the reaction. Fig. 3 shows the results obtained when S is equal to 0.5, i.e., $R_{diff} = 1.5$, and the reactant ratio in the feed, R^0, is varied between 1.1 and 3.0. When R^0 is equal to R_{diff}^0, i.e., $R^0 = R_{diff}^0 = 1.5$, R remains constant for all conversions.

On the other hand, when R^0 is not equal to R_{diff}^0, R deviates from R^0 as the reaction proceeds in the reactor. For example, when R^0 is larger than R_{diff}^0, e.g., $R^0 = 2.0$, R increases with the conversion because residual amounts of hydrogen, which has not been consumed during the reaction, are accumulated in the reactor. On the contrary, when R^0 is smaller than R_{diff}^0, e.g., $R^0 = 1.1$, R decreases with
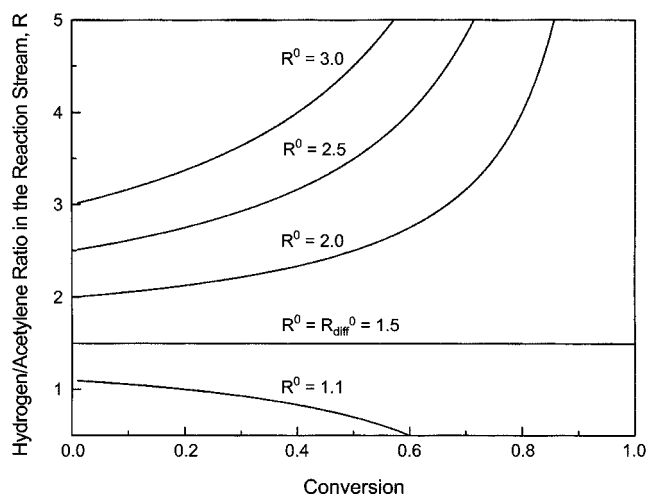
Fig. 3. Variation in the hydrogen/acetylene ratio in the reaction stream, R, with acetylene conversion when ethylene selectivity is constant, 0.5.

Fig. 5. Variation in the hydrogen/acetylene ratio in the reaction stream, R, with acetylene conversion for Catalysts A and B.
Solid lines: Catalyst A, Dotted lines: Catalyst B

the conversion because hydrogen is excessively consumed and therefore the reaction stream is depleted of hydrogen by the reaction. The deviation of R from R^0 becomes significant when the difference between R^0 and R^0_{diff} is large and the conversion approaches unity. Such a large increase of R should be avoided in industrial operation because the ethylene selectivity is lowered and consequently the acetylene loss increases when R is large [Huang, 1979].

2. Variable Selectivity

The assumption of constant S, adopted in the previous section, is not appropriate in practical processes because S changes with the reactant composition, particularly R, as illustrated for the above sample catalysts. Accordingly, we have calculated R at different conversions using S-R relations obtained for the sample catalysts.

Fig. 4 compares R-x relations for Catalyst A and constant S(=1.0). The deviation of R from R^0, occurring when R^0 mismatches with R^0_{diff}, is smaller for Catalyst A than for constant S. This result can

be explained as follows. R increases with the conversion when R^0 is larger than R^0_{diff}. On Catalyst A, the increase of R lowers the ethylene selectivity and consequently enhances the consumption of hydrogen per converted acetylene. Accordingly, the partial pressure of hydrogen in the reaction stream is lower for Catalyst A than for constant S even at the same conversion. The above analysis results indicate that the hydrogen/acetylene ratio, R, in the reaction stream is self-adjusted showing a regressive behavior when S decreases with R.

In Fig. 5, the deviation of R from R^0 is larger for Catalyst B than for Catalyst A when R^0 mismatches with R^0_{diff}. Accordingly, the self-adjustment of R by regression is more significant when the selectivity decreases more steeply with R, which is the case for Catalyst A than for Catalyst B.

We have also compared changes in the selectivity with the conversion, i.e., the S-x relation, for two sample catalysts, which are shown in Fig. 6. The selectivity significantly decreases with the con-
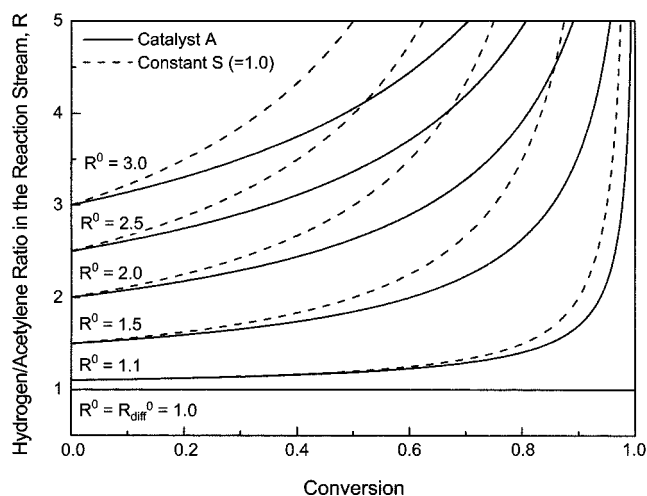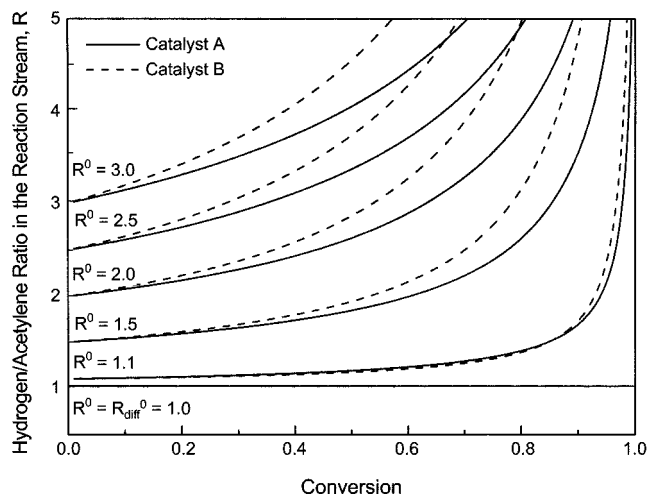

Fig. 4. Variation in the hydrogen/acetylene ratio in the reaction stream, R, with acetylene conversion for Catalyst A and constant S (=1.0).
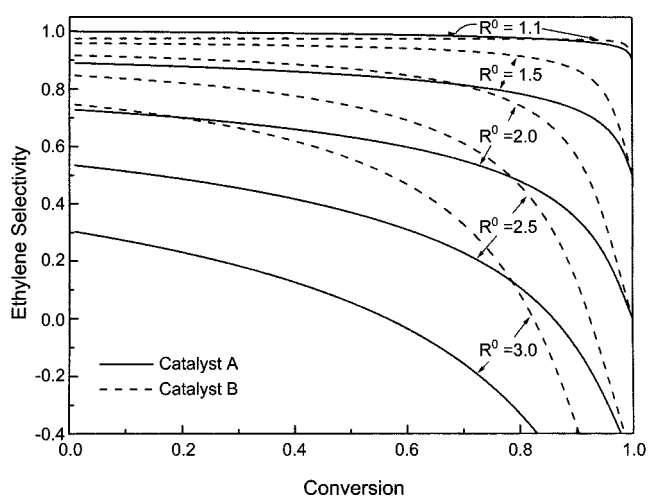Solid lines: Catalyst A, Dotted lines: Constant S

Fig. 6. Variation in ethylene selectivity, S, with acetylene conversion for Catalysts A and B.
Solid lines: Catalyst A, Dotted lines: Catalyst B

version, particularly when the mismatch between R^0 and R^0_{diff} is large and the conversion approaches unity. The selectivity drop is smaller for Catalyst A than for Catalyst B even when the initial selectivity is the same. This is notable by comparing the curve for Catalyst A at $R^0=2.0$ and the curve for Catalyst B at $R^0=3.0$, both of which have an initial S value of about 0.75. The difference in the rate of the selectivity drop between two catalysts occurs for two reasons. First, the hydrogen/acetylene ratio required for obtaining the initial S value of 0.75 is smaller for Catalyst A ($R^0=2.0$) than for Catalyst B ($R^0=3.0$), and therefore smaller amounts of hydrogen are consumed and R changes more slowly with the conversion for Catalyst A. Second, the regressive behavior of R is larger for Catalyst A than for Catalyst B, which again causes a slower change in R for Catalyst A.

CONCLUSIONS

Based on a reactor analysis and relation between the ethylene selectivity and the reactant composition, we have obtained the following conclusions about the performance of an integral reactor for acetylene hydrogenation. The hydrogen/acetylene ratio, R, in the reactor is self-adjusted by regression when S depends on R, and the regressive behavior of R is greater when S decreases more steeply with R. Control of the hydrogen/acetylene ratio, R^0, close to the differential reactant ratio, R^0_{diff}, the latter being determined by S, at the reactor inlet is the most essential to the operation of the process at high ethylene selectivity. This study also indicates that catalysts showing high ethylene selectivity over a wide range of the $P_{H_2}/P_{C_2H_2}$ ratio are required for the design of a highly selective hydrogenation process.

APPENDIX I. DERIVATION OF A RELATION BETWEEN S AND R

The rates of individual reaction steps described in Fig. 1 are expressed as follows.

$$\frac{d\theta_H}{dt} = 2k_1 \cdot P_{H_2} \cdot \theta_S^2 - k_1^{-1} \cdot \theta_H^2 - k_3 \cdot \theta_{C_2H_2} \cdot \theta_H^2 - k_5 \cdot \theta_{C_2H_4} \cdot \theta_H^2 \tag{7}$$

$$\frac{d\theta_{C_2H_2}}{dt} = k_2 \cdot P_{C_2H_2} \cdot \theta_S^2 - k_3 \cdot \theta_{C_2H_2} \cdot \theta_H^2 \tag{8}$$

$$\frac{d\theta_{C_2H_4}}{dt} = k_4^{-1} \cdot P_{C_2H_4} \cdot \theta_S + k_3 \cdot \theta_{C_2H_2} \cdot \theta_H^2 - k_5 \cdot \theta_{C_2H_4} \cdot \theta_H^2 - k_4 \cdot \theta_{C_2H_4} \tag{9}$$

$$\frac{d\theta_{C_2H_6}}{dt} = k_5 \cdot \theta_{C_2H_4} \cdot \theta_H^2 - k_6 \cdot \theta_{C_2H_6} \tag{10}$$

$$\frac{dP_{H_2}}{dt} = k_1^{-1} \cdot \theta_H^2 - k_1 \cdot P_{H_2} \cdot \theta_S^2 \tag{11}$$

$$\frac{dP_{C_2H_2}}{dt} = -k_2 \cdot P_{C_2H_2} \cdot \theta_S^2 \tag{12}$$

$$\frac{dP_{C_2H_4}}{dt} = k_4 \cdot \theta_{C_2H_4} - k_4^{-1} \cdot P_{C_2H_4} \cdot \theta_S \tag{13}$$

$$\frac{dP_{C_2H_6}}{dt} = k_6 \cdot \theta_{C_2H_6} \tag{14}$$

Using a steady-state approximation for the reaction rates of intermediate species, we obtain the following correlation among fractions of the surface species.

$$2k_1 P_{H_2} \theta_S^2 = (k^{-1} + k_3 \theta_{C_2H_2} + k_5 \theta_{C_2H_4})\theta_H^2 \tag{15}$$

$$\theta_{C_2H_2} = \frac{k_2}{k_3} P_{C_2H_2} \frac{\theta_S^2}{\theta_H^2} \tag{16}$$

$$\theta_{C_2H_4} = \frac{k_4^{-1} P_{C_2H_4}\theta_S + k_2 P_{C_2H_2}\theta_S^2}{k_4 + k_5\theta_H^2} \tag{17}$$

$$\theta_{C_2H_6} = \frac{k_5}{k_6}\theta_{C_2H_4}\theta_H^2 \tag{18}$$

Solving these correlations referred to θ_H, we can obtain the following equation.

$$(k_1 k_5)\theta_H^4 + (k_1 k_4 + k_4^{-1} P_{C_2H_4}\theta_S + 2k_2 k_5 P_{C_2H_2}\theta_S^2 - 2k_1 k_5 P_{H_2}\theta_S^2)\theta_H^2$$
$$- 2k_1 k_4 P_{H_2}\theta_S^2 + k_2 k_4 P_{C_2H_2}\theta_S^2 = 0 \tag{19}$$

The selectivity is given as follows from Eq. (12) and (13).

$$S_{diff} = \frac{\dfrac{dP_{C_2H_4}}{dt}}{-\dfrac{dP_{C_2H_2}}{dt}} = \frac{k_4 \times \theta_{C_2H_4} - k_4^{-1} \times P_{C_2H_4} \times \theta_S}{k_2 \times P_{C_2H_2} \times \theta_S^2} \tag{20}$$

We assumed that the surface fraction of vacant sites, θ_S, was constant because the surface was covered mostly by hydrocarbons and hydrogen during the reaction. In other words, the exposed surface fraction of vacant sites is relatively small, and consequently the influence of reactant partial pressures on θ_S is negligible. Combining Eqs. (15)-(19) for the surface variables with the above Eq. (20) for the selectivity, we can express the selectivity as a function of partial pressures of the species involved in the reaction. The following Eq. (21) is a general expression for the selectivity, S, in terms of the $P_{H_2}/P_{C_2H_2}$ ratio, R.

$$S = A - \frac{B}{C + D \times R + \sqrt{E + F \times R + G \times R^2}} \tag{21}$$

APPENDIX II. EXPERIMENTAL PROCEDURE OF ACETYLENE HYDROGENATION

Two sample catalysts were used in this study: a commercial Pd-

Table 2. Operating conditions of G.C.

Column	1/8 in×7.0 m (Porapak N: 80/100 mesh)
Column temperature	323 K
Injector temperature	333 K
Detector temperature	473 K
Carrier (N_2) flow rate	0.42 cm^3/sec
Air flow rate	5 cm^3/sec
H_2 flow rate	0.5×cm^3/sec
Detector	FID

Ni/α-Al$_2$O$_3$ catalyst (Catalyst A), and a promoted catalyst prepared in this laboratory (Catalyst B). Details of the catalyst preparation, particularly for Catalyst B, are given in our previous reports [Shin et al., 1998, 2002]. Acetylene hydrogenation was performed at 373 K in a pyrex micro-reactor at atmospheric pressure, using a gas mixture containing 0.65% acetylene in ethylene prepared by the Korea Research Institute of Standard and Science. The hydrogen/acetylene ratio in the reaction stream was varied from 1.0 to 4.0, and the space velocity was controlled between 66.7 and 267 cm^3/g·sec to obtain different acetylene conversions. Reaction products were analyzed with an on-line G.C. (Gow-Mac, model 750 with FID) using Porapak N as a column material. The conditions of G.C. operation are given in Table 2. The ethylene selectivity was calculated from the G.C. analysis results, which gave the amounts of converted acetylene and produced ethylene.

NOMENCLATURE

Superscript "0": reactor inlet

P_m : partial pressure of species "m"

R : hydrogen to acetylene ratio in the reaction stream ($=P_{H_2}/P_{C_2H_2}$)

R_{diff} : differential hydrogen/acetylene ratio for converted reactants ($=$rate of hydrogen consumption/rate of acetylene consumption$=dP_{H_2}/dP_{C_2H_2}$)

S : ethylene selectivity ($=$moles of produced ethylene/mole of converted acetylene$=-dP_{C_2H_4}/dP_{C_2H_2}$)

t : reaction time

x : acetylene conversion

θ_i : surface coverage of species "i"

k_j : rate constant of reaction step "j"

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