Kinetic Study of Simultaneous Ethanol Decomposition and Reduction of Low-grade Iron ore at Transient Temperature

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Abstract. An ethanol-assisted ironmaking method had previously been proposed, resulting in a significantly lower temperature of iron reduction. However, the kinetic mechanism remains unknown. A kinetic model for transient temperature condition was introduced, then numerically solved and curve-fitted to the experimental data using MATLAB software. There were 8 main reactions involved: (1) decomposition of ethanol, (2) decomposition of methane, (3) steam reforming of methane, (4) water-gas shift, (5) Boudourd reaction, (6) direct reduction by C, (7) indirect reduction of iron oxide by CO, and (8) iron reduction by H₂. Curve fitting methods were successfully conducted with satisfying results (R² > 0.90) calculating three parameters consisting of reaction rate constants, activation energies, and diffusion factors of each reaction. The interpretation of the calculated diffusion factors reveals that the reaction of gases inside pore might be inhibited by carbon deposition on the pore surface of iron ore. It revealed that the direct reduction by C predominates the overall reduction process.

1. Introduction
The light alcohol, such as ethanol is a prominent candidate as a reducing agent for ironmaking [1]. Not only is it less hazardous, but it can be produced from a variety of biomass sources. Its use could lead to a decrease in CO₂ emissions. Currently, bioethanol is produced by the fermentation of sugar cane, corn grains, and other starch-rich materials, and is a mature technology [2]. Recent researchers have focused on producing bioethanol from lignocellulosic biomass, the so-called second-generation bioethanol. Ethanol production from lignocellulose would open the possibility for the utilization of different and low-cost biomass, such as agricultural wastes and forestry residues (e.g., straw, grasses, corn stover, and wood); in this way, a competition of energy-food production from agricultural sources would be avoided [3]. Another remarkable finding of ethanol production from gas fermentation, recently, is also getting more attractive to be implemented. Ethanol recovery like Lanzatech process, utilize the tail gas of iron and steelmaking processes might be one approach to realize the idea to ensure ethanol security as ironmaking fuel [4]. More approaches are required to evaluate the benefit of ethanol utilization as a reduction agent for ironmaking.

On the other hand, the abundance of goethite over hematite and magnetite ore needs more attention to be effectively utilized. Goethite, is a low-grade iron ore containing high combined water, requires more energy for converting it to hematite through a dehydration process before reduction [5]. For compensating the energy requirement for a dehydration process, the iron reduction reaction should be faster or proceeded at a lower temperature. Figure 1 shows the proposed process of ethanol-assisted ironmaking utilizing the porous iron ore from goethite dehydration as raw material. In the system of
simultaneous ethanol decomposition and iron reduction, ethanol acts as a reducing agent for iron oxide, meanwhile the iron oxide acts as a catalyst for ethanol decomposition producing H$_2$ and CO.

As reported in [1], ethanol reduces the iron oxide at a significantly lower temperature compared to coke-iron oxide reaction. However, the reaction mechanisms are still unclear. As one approach, the porous iron ores is submitted to a programmed transient temperature condition (with a constant heating rate) while a reducing gas mixture flows over it. This method has been commonly known as a temperature-programmed reduction (TPR) [7]. The current study is aimed to reveal the mechanism of the reaction during the simultaneous ethanol decomposition and iron reduction process through kinetic simulation and data curve-fitting.

![Figure 1. Mechanism scheme of ethanol decomposition – iron reduction as concluded in [1]](image)

2. Experimental Methods

2.1. Ethanol decomposition and iron reduction in temperature-programmed reaction

Australian goethite (GE) ore with the total Fe content of 57wt% and combined water (CW) of 8.6wt% was employed in this study. The original ore was sieved so that the particle size range from 1 to 2 mm. The porous ore was already prepared by dehydrating the original one at 300 °C with a heating rate of 3 °C min$^{-1}$ and kept for 24 h under air atmosphere, as mentioned in the previous study [1]. The reduction experiment was conducted by reducing 0.3 g of dehydrated low-grade iron ore in a quartz tube reactor (ID of 6 mm) under an inert Ar atmosphere. The reactor was heated in a vertical infrared furnace to reach final temperature (900 °C) at a heating rate of 10 °C min$^{-1}$. Ethanol reagent (99.5 vol%) at 0.04 ml min$^{-1}$ was drop-wise introduced into the iron ore bed in the reactor during heating up. The outlet reactor gases were analyzed in-line using quadrupole mass spectroscopy (QMS200, Pfeiffer).

2.2. Sample Analysis and Characterizations

2.2.1. Gas Analysis. The outlet reactor gases, such as C$_2$H$_5$OH, H$_2$, CH$_4$, CO, CO$_2$, and H$_2$O were analyzed using quadrupole mass spectroscopy (QMS200, Pfeiffer). The evolution of total outlet gas flowrate was also monitored and recorded using a gas flowmeter. The molar flowrates of each gas were calculated as in our previous study [1] using (1).

$$\dot{n}_i = 41571.74 f_T C_i$$

The factor of 41571.74 is the conversion factor of gas volumetric flowrate to molar flowrates at NTP - Normal Temperature and Pressure - condition [µmol Nml$^{-1}$]. The NTP condition is defined as 20°C and 1 atm.

2.2.2. Reduction degree (RD) calculation. Characteristics of the ore structures and compositions before and after the reactions were analyzed using X-ray powder diffractometry (XRD; Miniflex, Rigaku). The reduction degree (RD) can be estimated as the molar percentage of the removed oxygen to the total removable oxygen in the sample. For instance, the RD of pure substances of Fe$_2$O$_3$, Fe$_3$O$_4$, FeO, Fe, and Fe$_3$C were considered as 0%, 11%, 30%, 100%, and 100%, respectively. As considering the presence of some gangue materials such as SiO$_2$, Al$_2$O$_3$, and other oxides within the ore samples. The RD of each sample was then calculated based on the composition of iron oxides in the sample using equation (2).

$$RD = \sum x_i RD_i$$

2.2.3. Carbon content analysis. The carbon content in the iron ore was calculated by the weight change of the iron ore after reduction using ethanol and after combustion at 1000 °C for 30 min under 500 ml
min of airflow. Considering the reoxidation of reduced iron ore to hematite, the carbon content was calculated using a similar method in our previous study [1].

2.2.4. Microscopic Analysis. To observe the deposition of carbon from ethanol in the pore of iron ore, carbon mapping cross-sectional analysis was conducted using a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) JEOL JSM-7400F. In addition, to confirm the nanoscale contacts between the deposited carbon and iron ore, transmission electron microscope (TEM) was taken using a JEOL JEM-2010 microscope at an operating voltage of 200 kV at the highest magnifications.

2.3. Kinetic analysis

2.3.1. Reaction modeling. Ethanol vapor decomposed rapidly in the presence of iron ore means that the catalytic reaction of ethanol decomposition occurs. Simultaneously, the Fe₂O₃ changes to metallic-Fe, the reduction occurs. In this approach, we proposed that there are eight main reactions involved, (r1) decomposition of ethanol (C₂H₅OH(g) → CH₄(g) + H₂O(g) + C); (r2) decomposition of methane (CH₄(g) → C(s) + 2H₂(g)); (r3) steam reforming of methane (CH₄(g) + H₂O(g) → CO(g) + 3H₂(g)); (r4) water gas shift reaction (CO(g) + H₂O(g) → CO₂(g) + H₂(g)); (r5) Boudard reaction (C(s) + CO₂(g) → 2CO(g)); (r6) Iron reduction by carbon (FeO(s) + xC(s) → Fe(s) + xCO(g); with x=1.5); (r7) Iron reduction by CO (FeO(s) + xCO(g) → Fe(s) + xCO₂(g); with x=1.5); (r8) Iron reduction by H₂ (FeO(s) + xH₂(g) → Fe(s) + H₂O(g); with x=1.5).

The reduction of FeOₓ can be assumed as an oxygen removal of from iron oxide. Those reactions can be simplified as ROₓ(s) + C(s) → CO(g); ROₓ(s) + CO(g) → CO₂(g); and ROₓ(s) + H₂(g) → H₂O(g) for (r6) direct reduction by C, (r7) reduction by CO, and (r8) reduction by H₂, respectively.

The kinetic equation with the second-order reaction at each reaction in term of the generation of component j is expressed as in (3).

\[ r_j = k_{overall \text{ix}} n_j n_k \]  \hspace{1cm} (3)

The mechanism includes the mass transfers of both reactants and products, in term of external diffusion and internal diffusion in the pore, the adsorption/desorption into the pore surface, and the surface reactions. In overall terms, introducing a resistance concept in reaction model would simplify the overall kinetic term as in (4)

\[ \frac{1}{k_{overall \text{ix}}} = \frac{1}{k_{dix}} + \frac{1}{k_{rix}} \]  \hspace{1cm} (4)

Mass transfer phenomena of gases into pore including internal and external diffusion are evaluated by the coefficient of apparent mass transfer effect on the overall kinetic, \( C_{d_j} \), for each component j. Thus, the overall kinetic term should be

\[ k_{overall \text{ix}} = C_{d_j} k_{rix} \]  \hspace{1cm} \begin{equation} C_{d_j} = \left( \frac{k_{di}}{k_{di}+k_{rix}} \right)_j \end{equation}  \hspace{1cm} (5)

Some assumptions were taken into consideration: (i) \( C_{d_j} \) was assumed as a constant. (ii) Since the iron ore bed (0.3 g) in the reactor (ID = 6 mm; H = 7 mm) is quite small, and with a preliminary experiment confirming the temperature is uniform at any axial position around the ore bed. In other meaning, reactions were assumed uniform at any positions in bed. In addition, since in the transient temperature condition, the equilibrium is not reached. Thus, the equilibrium constant was not taken into consideration.

In the complex system, the overall rate generation of component j can be expressed
An Arrhenius-type overall kinetic equation was used to model $k_{r\text{ix}}$ expressing

$$k_{r\text{ix}} = k_{fr0\text{ix}} \exp \left( -\frac{E_{a\text{ix}}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right)$$

(7)

The term of \( \left( \frac{1}{T} - \frac{1}{T_0} \right) \) in the overall kinetic equation was introduced to improve the independency of each parameter during curve fitting.

Under the transient temperature state with a heating rate $\beta = \frac{dT}{dt}$ (i.e., 10 K min$^{-1}$), the mole balance of each components $j$ can be expressed as (8)

$$\frac{dn_j}{dT} = \frac{1}{\beta} \left( \dot{n}_{j0} + C_{dj} \sum k_{r\text{ix}} n_j n_k \right)$$

(8)

In the case of ethanol, initial molar amount, $\dot{n}_{j0}^{c_2H_5O_H}$ is 686 μmol min$^{-1}$, while for other product gases, the $\dot{n}_{j0} = 0$, respectively.

2.3.2. Curve fitting procedures. As in (8), 24 parameters were estimated, consists of eight kinetics constants of reactions at $T_0$ (= 750 °C), $k_{fr10} \sim k_{fr80}$, eight activation energies, $E_{a1} \sim E_{a8}$, and eight coefficients of the mass transfer effect, $C_{dA} \sim C_{dH}$. These parameters were estimated by a curve fitting method using the sum square error (SSE) as the objective function. Considering the SSE should be not containing any units. Thus, the unitless SSE was introduced in the fitting as in (9).

$$\overline{\text{SSE}} = \sum \left( \frac{n_{j\text{calc}} - n_{j\text{data}}}{n_{j\text{data}}} \right)^2$$

(9)

Numerical solution for (8) was performed in MATLAB®. Numerical integration for the simultaneous ordinary differential equation of (8) was calculated using “ode15s” function. Curve fitting was performed by running an optimization program to minimize the $\overline{\text{SSE}}$ value of 26 data points in (9) using “lsqnonlin” function with iteration parameters “TolX” = 1e-10; “TolFun” = 1e-10; “MaxIter” = 8000; “MaxFunEvals” = 10000. Initial guess value of the parameter $k_{r10} \sim k_{r80}, E_{a1} \sim E_{a8}, C_{dA} \sim C_{dH}$, were $10^3, 10^5, \text{ and } 0.5$, respectively. The lower boundaries for all parameters were set as zero. The goodness of fit using $R^2$ were also calculated.

3. Results and Discussions

3.1. Simultaneous ethanol decomposition and iron reduction

This study utilized the data of simultaneous ethanol decomposition with iron reduction reaction that previously reported in [1]. The raw data was then reorganized to find a correlation between kinetic activity and oxide structure in the ore as depicted in Figure 2. These data can be interpreted briefly that significant ethanol decomposition is started at 300 °C, together with iron reduction by CO (Fe$_2$O$_3$ + CO → Fe$_3$O$_4$ + CO$_2$). At 400 °C, Iron reduction by H$_2$ is started (Fe$_2$O$_3$ + H$_2$ → Fe$_3$O$_4$ + H$_2$O, and Fe$_3$O$_4$ + H$_2$ → FeO + H$_2$O). At 600 ~ 700 °C, the ethanol decomposition seems slower when iron ore structure change from Fe$_3$O$_4$ to FeO. Above 700 °C, significant iron reduction by deposited-C is started (FeO + C = Fe + CO). It is remarked by as C content increasing, the RD and CO increase significantly. While there is no significant generation in H$_2$O from reduction by H$_2$ and CO$_2$ from reduction by CO.
Figure 2. Simultaneous ethanol decomposition-iron reduction of dehydrated goethite ore in [1]. Data were reorganized for kinetic analysis.

3.2. Curve fitting results

RD and carbon contents in the ore are only evaluated at 100 °C intervals. Since the RD is expressed in molar percentage, it is difficult to use in the kinetic calculation. Thus, the term of removed oxygen (RO) was introduced to describe the remaining amount of removable oxygen in the iron oxide component. The initial RO (as hematite content in the ore) and carbon amount of the iron ore were 718 and 0 µmol, respectively. The RO and carbon content are both expressed as the accumulated amount (i.e., in molar unit). The gas flowrate data were obtained in the expression of the mole amount per time unit (e.g., in the unit of µmol min⁻¹). To arrange the same unit order of all measured component amount, the molar flowrate data of the generated gases j were reformed into the accumulated molar amount of gas using

\[ n_{j,T_i}^{acc} = n_{j,T_{i-1}}^{acc} + \sum_{l=2}^{i} \frac{T_{i}+T_{i-1}}{2\beta} (\dot{n}_{j,T_i} + \dot{n}_{j,T_{i-1}}) \quad \text{with } i = \text{index of data point} \]  

Figure 3 shows the curve fitting result of each component in the accumulated molar amounts. In addition, to demonstrate the reduction behavior, the simulated RO was then converted back to RD. Based on the goodness of fit, R², the proposed model was satisfactorily fit to the data for H₂O, C, RD, CO, H₂, and C₂H₅OH. However, it was quite fit CH₄ and CO₂. Based on the curve shape of RD compared to the amount of C, H₂, and CO, as the reducing agent. The RD is found strongly correspond with the carbon amount, especially at the temperature higher than 700 °C, and slightly with H₂ and CO, even if the H₂ and CO are abundantly present during the ethanol decomposition process. A previous study [8] mentioned that the increase of RD corresponds to the existence of H₂ and CO, which are dominate the reduction process. However, the reduction by H₂ is tended to a constant rate at the temperature higher than 450 °C [9]. The reduction by H₂ and CO seems to have an effect at the lower temperature only. Understanding the reduction behavior under simultaneous process is complicated to observe. In our approach, the simulation calculated the rate constant of the proposed reaction model obtaining the parameters of the rate constant \( k_{fr01} \) and activation energy \( E_{at1} \) of each reaction were listed in Table 1.
Figure 3. Component molar accumulated data and the model curve fitting results. The $R^2$ close to 1 means the model almost fits to experimental data.
The $k_{fro1}$ is evaluated for $T_0 = 750$ °C, meaning that all $k_{fro1}$ simulate the rate of each reaction at 750 °C. These values describe the predominant reactions occur during the simultaneous ethanol decomposition and iron reduction process. The higher values of $k_{fro1}$, the more dominating reaction is. As in the ethanol decomposition, ethanol decomposed into CH$_4$, H$_2$O, and deposited C. The reaction then immediately proceed to the steam reforming generating H$_2$ and CO, and water gas shift reaction generating more H$_2$ and CO$_2$. However, a near-zero value of $k_{fro1}$ for Boudoard reaction indicates that Boudoard reaction does not occur in this process since the reaction temperature for Boudoard reaction requires higher than 800 °C [12]. Meanwhile, upon the iron reduction, it is obvious that at 750 °C the iron reduction by carbon predominates the overall reduction process. It seems that the iron reduction by H$_2$ and CO have no significant effect above this temperature. The activation energies obtained from this study were then found mostly agreed in comparison to the other references data, which were evaluated from other non-simultaneous reaction studies.

### Table 1. Obtained parameters of reaction kinetic from curve fittings using MATLAB

| No | Reactions | $k_{fro1}$ at 750 °C [1/min.mol] | $E_a$ [kJ/mol] | $E_{ai}$ [kJ/mol] | References |
|----|-----------|--------------------------------|----------------|----------------|-------------|
| 1  | Decomposition of ethanol: C$_2$H$_5$OH(g) $\rightarrow$ CH$_4$(g) + H$_2$O(g) + C | 0.346 | 1.77 | 1.87~16.8 | [10] |
| 2  | Decomposition of methane: CH$_4$(g) $\rightarrow$ C(s) + 2H$_2$(g) | 0.199 | 25.23 | 60 | [11] |
| 3  | Steam reforming: CH$_4$(g) + H$_2$O(g) $\rightarrow$ CO(g) + 3H$_2$(g) | 0.747 | 127.05 | 169.5 | [12] |
| 4  | Water gas shift reaction CO(g) + H$_2$O(g) $\rightarrow$ CO$_2$(g) + H$_2$(g) | 1.41 | 51.65 | 45 | [13] |
| 5  | Boudoard reactions: C(s) + CO$_2$(g) $\rightarrow$ 2CO(g) | $1.82\times10^{-9}$ | 123.02 | 120~310 | [14] |
| 6  | Iron reduction by C: FeO(s) + xC(s) $\rightarrow$ Fe(s) + xCO(g); x=1.5 | 0.051 | 139.24 | 280 | [15] |
| 7  | Iron reduction by CO: FeO(s) + xCO(g) $\rightarrow$ Fe(s) + xCO$_2$(g); x=1.5 | $1.35\times10^{-3}$ | 118.91 | 116~151 | [16] |
| 8  | Iron reduction by H$_2$: FeO(s) + xH$_2$(g) $\rightarrow$ Fe(s) + H$_2$O(g); x=1.5 | $6.83\times10^{-4}$ | 99.68 | 61.5~71 | [17] |

#### 3.3 Interpretation of parameter $C_{dj}$:

Table 2 shows the obtained parameters of $C_{dj}$ from the curve fittings. The parameter of $C_{dj}$ was introduced to compensate for the unknown effect of ore particle size, surface area, etc. as well as mass transfer effect through simultaneous surface reaction occurs. $C_{dj}$ in this term correlates with the mass transfer properties of each reacted components. $C_{dj}$ could be also introduced as Thiele modulus describing the relationship between diffusion and reaction rate in porous ore with no mass transfer limitations. Thiele modulus is generally used in determining the effectiveness factor for catalyst pellets [18]. This approach is set according to assumptions of the diffusion through a surface film is very fast compared to diffusion into the grain interior.

The overall generation of RO, H$_2$O, and CO are controlled by the reaction, which corresponds to the reduction process by C and H$_2$. Meanwhile, the generation of other components, specifically the deposited carbon and CH$_4$ are controlled by diffusion that might correspond to the ethanol decomposition reaction, steam reforming, and water gas shift taking place inside the ore. Since it was difficult to distinguish the contribution of each reaction in the component generation, the interpretation of $C_{dj}$ might be limited to the overall generation of the component only. The factors of mass transfer $C_{dj}$...
is only considered as a constant, however, it might be a function of temperature as well to correlate with the effect of sintering phenomena at higher temperature reaction, pore. This will be left for further investigations.

Table 2. The obtained parameters of $C_{dj}$ from the curve fitting result

| Components, $j$          | Obtained $C_{dj}$ | Thiele modulus, $\varphi \approx \frac{(1-C_{dj})}{C_{dj}}$ | Interpretation: Overall generation of component $j$ is controlled by |
|--------------------------|-------------------|----------------------------------------------------------|------------------------------------------------------------------|
| Removed Oxygen, RO       | 0.8662            | 0.15                                                     | Reaction                                                         |
| H$_2$O                   | 0.6707            | 0.49                                                     | Reaction                                                         |
| CO                       | 0.6083            | 0.64                                                     | Reaction                                                         |
| C-deposited              | 0.2046            | 3.89                                                     | Diffusion                                                        |
| C$_2$H$_5$OH             | 0.0437            | 21.89                                                    | Diffusion                                                        |
| CH$_4$                   | 0.0403            | 23.84                                                    | Diffusion                                                        |
| H$_2$                    | 0.0236            | 41.43                                                    | Diffusion                                                        |
| CO$_2$                   | 0.0206            | 47.34                                                    | Diffusion                                                        |

In addition, using cross-sectional SEM-EDS observation (Figure 4), it was confirmed that carbon from ethanol decomposition deposited inside iron ore through diffusion in its pore. At the lower temperature (400 °C), the deposited carbon seems only concentrates on some points. Then, as temperature elevated (700 °C), it continues to be accumulated and homogenously distributed inside the iron ore, meaning that the contact between carbon and iron oxide for reduction can proceed in all part of iron ore. TEM observation at the iron ore sample after reduction with ethanol at 750 °C is shown in Figure 5. The TEM image consists two contrast colors: the dark grey (or close to black) one corresponds to the higher density component (i.e., Fe), and the transparent one corresponds to carbon. It confirms that the surface of iron ore is already covered by amorphous carbon in a nano-scaled contact that allows the significant iron reduction by carbon (direct reduction) causing the iron reduction by carbon predominates the overall reduction process. It can be also interpreted that the deposited carbon also might inhibit H$_2$ and CO to effectively reduce the iron ore. This phenomenon corresponds with the reaction rate of the iron reduction by H$_2$ and CO found lower than the reduction by C; nevertheless, the activation energy of reduction by C is the highest among other reaction.

![Figure 4](image1.png)  ![Figure 5](image2.png)
As an overall evaluation, the transient state kinetic study can provide more details information about the main mechanisms of simultaneous ethanol decomposition and iron reduction over low-grade iron ore. This result contributes to a significant improvement in our understanding of what we found in our previous study in [1]. It reveals that even if H₂ and CO are significantly generated from a complex reaction during ethanol decomposition, the iron reduction by H₂ and CO seems only act at the temperature lower than 750 °C. At above the temperature, the reduction by carbon (direct reduction) predominates the overall reduction process. However, further studies need to be done in order to investigate the other parameters to extend the accuracy of the proposed reaction model. This study confirms the one benefit from kinetic aspect to implement the ethanol-assisted iron reduction process for future ironmaking.

Conclusions
Ethanol, counted as a carbon-free product from biomass, is a prominent candidate to substitute the reducing agent for ironmaking, instead of the depleting coal-based coke. The kinetic study is necessary for understanding the mechanism of the simultaneous ethanol decomposition – iron reduction process. Curve fitting method was successfully demonstrated with satisfying results (R²>0.90) calculating 24 parameters consisting k_{r_{0i}}, E_{ai}, and C_{dj}. There were 8 main reactions involved: (i) decomposition of ethanol, (ii) decomposition of methane, (iii) steam reforming of methane, (iv) water gas shift, (v) Boudoord reactions, (vi) iron reduction by C, (vii) iron oxide reduction by CO, and (vii) iron reduction by H₂. However, it seems Bourdood reaction does not occur during the process. The reduction by H₂ and CO proceeds from lower temperature. Meanwhile reduction by deposited C (direct reduction) occurs at higher temperature as well as the deposited carbon is accumulated covering the pore surface. The interpretation of the obtained parameters C_{dj} shows that the reaction of gases inside pore might be inhibited by carbon deposition on the pore surface of iron ore.

Nomenclatures
Symbols
\( \beta \) : heating rate of the transient system [K min⁻¹]
\( C_i \) : the gas molar fraction of each component \( i \) measured by QMS200 [-]
\( E_{ai} \) : the activation energy of reaction \( i \) [J mol⁻¹];
\( f_r \) : total volumetric flowrate in the reactor outlet gas [Nml min⁻¹]
\( k_{overall \ i x} \) : overall rate coefficient in bulk reaction \( i x \), with
\( k_{dix} \) : coefficients of mass transfer including external diffusion and internal diffusion in the pore
\( k_{ri} \) : rate coefficients of reactions (surface reaction) [mol¹ s⁻¹];
\( k_{r_{0i}} \) : rate coefficient of forward reaction \( i x \) at \( T_0 \) [mol¹ s⁻¹];
\( n_j, n_k \) : molar amounts of components \( j \) and \( k \) [mol].
\( \dot{n}_j \) : the calculated molar flowrate of each components \( i \) (i.e., C₂H₅OH, H₂, CH₄, CO, CO₂, H₂O) [µmol min⁻¹]
\( \dot{n}_{j0} \) : the molar flowrate of gas entering the reactor [µmol min⁻¹]
\( R_D_j \) : reduction degree of the different iron structures [mol%]
\( R \) : the ideal gas constant [=8.314 J mol⁻¹K⁻¹]
\( T, T_0 \) : temperature [K] and the reference temperature [K], respectively
\( x_{jc} \) : mass fraction of iron oxide component \( j \) (jc = Fe₂O₃, Fe₃O₄, FeO, Fe, or Fe₃C) in the sample according to the intensity of X-rays diffracted by a selected plane (hkl) of each component, calculated based on the reference intensity ratio (RIR) methods

Subscripts
\( i x \) : reaction number (1 to 8)
\( j, k \) : components indices related to reaction \( i \) (e.g., RO, C, CO, CO₂, H₂, H₂O, CH₄, C₂H₅OH), respectively.
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