Effect of P$_2$O$_5$ Addition on the Rate of CO$_2$ Dissociation on the Surface of Fe$_{1}$O-base Molten Oxides

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For clarification of the surface active effect of P$_2$O$_5$ in the reaction kinetics and mechanism of the various metallurgical processes, the effect of P$_2$O$_5$ addition on the reaction rate of CO$_2$, dissociation on the surface of the Fe$_{1}$O, Fe$_{1}$O–CaO (mol%Fe$_{1}$O : mol%CaO = 6 : 4), Fe$_{1}$O–SiO$_2$ (mol%Fe$_{1}$O : mol%SiO$_2$ = 7 : 3), and Fe$_{1}$O–CaO–SiO$_2$ (mol%Fe$_{1}$O = 35, mol%CaO/mol%SiO$_2$ = 1.13–1.27 and 1.36–1.47) melts was investigated at 1 773 K with P$_{CO_2}$/P$_{CO}$ = 1 by using isotope exchange technique. The rate constant decreased with increasing P$_{CO_2}$ content of melts and the residual rate constant was observed at high P$_{CO_2}$ content. However, the change of the Fe$^{3+}$/Fe$^{2+}$ ratio of molten oxide was not observed. Results were analyzed by using "site blockage model" of P$_{2}$O$_{5}$, and it was concluded that the rate controlling step of CO$_2$ dissociation was the dissociation reaction of adsorbed CO$_2$ molecule on the surface of molten oxides.

KEY WORDS: kinetics; reaction mechanism; isotope exchange technique; molten oxide; P$_2$O$_5$; surface active effect.

1. Introduction

The CO–CO$_2$ gas reaction with molten oxides is the essential reaction in numerous metallurgical refining processes and the refining speed depends on this reaction rate. Therefore, the kinetic data of CO–CO$_2$ reaction are important for the analysis, simulation and the development of refining processes. Especially in the ironmaking and steelmaking processes, for development of the bath smelting process as an innovative process, this reaction rate has been widely investigated by many researchers$^{1}$–$^{13}$) and the reduction rate of molten oxides containing iron oxide is expressed as the function of temperature and the Fe$^{3+}$/Fe$^{2+}$ ratio of the molten oxides. However, this relationship cannot be applied when the strong surface active elements such as P$_2$O$_5$ or Na$_2$O are contained in molten oxides.

Pal$^{14}$) measured the reduction rate of PbO by N$_2$–H$_2$ gas in molten PbO–SiO$_2$ melts at the temperature range from 1 123 to 1 273 K by thermogravimetric method and the rate decreased by the addition of P$_{2}$O$_{5}$. Nagasaka$^{10}$) investigated the effect of many kinds of additives on the reduction rate of molten iron oxide with CO gas and reported that the effect of P$_{2}$O$_{5}$ addition could not be expressed by the composition of molten oxides. Sun$^{12}$) measured the dissociation rate of CO$_2$ on the molten Fe$_{1}$O at 1 673 K by $^{13}$CO$_2$–CO isotope exchange technique and the small amount of P$_{2}$O$_{5}$ addition decreased the rate. However, limited data can be available for the quantitative evaluation of the surface active effect of P$_{2}$O$_{5}$ on the reaction rate and for discussion of reaction mechanism.

From this point of view, in the present work the effect of P$_{2}$O$_{5}$ addition on the dissociation rate of CO$_2$ on the surface of molten oxides containing iron oxide has been investigated by using $^{13}$CO$_2$–CO isotope exchange technique$^{15}$) at 1 773 K and the reaction mechanism has been discussed.

2. Experimental

2.1. Principle

In the isotope exchange technique, the exchange reaction rate of isotope gas species between two molecules is measured. In the present study, CO–CO$_2$ mixture gas (CO : CO$_2$ = 1 : 1) containing $^{13}$CO$_2$ is used, therefore $^{13}$CO$_2$, $^{12}$CO$_2$ and $^{12}$CO are mainly contained in inlet gas and the exchange reaction (1) occurs on the surface of molten oxides,

$^{13}$CO$_2$ + $^{12}$CO = $^{13}$CO + $^{12}$CO$_2$ \hspace{1cm} (1)

This reaction is divided into two elementary reactions as Eqs. (2) and (3).

$^{13}$CO$_2$ = $^{13}$CO + O \hspace{1cm} (2)

$^{12}$CO + O = $^{12}$CO$_2$ \hspace{1cm} (3)

Accordingly, the dissociation rate of CO$_2$ can be observed by measuring the formation rate of $^{13}$CO or consumption rate of $^{13}$CO$_2$. In this method, reaction (1) does not affect the CO–CO$_2$ ratio of reaction gas, therefore the reaction rate can be measured under the condition that the molten oxide is in equilibrium with CO–CO$_2$ gas. Then, the effect
of the liquid phase mass transfer can be eliminated and the interfacial chemical reaction rate can be observed. The reaction constant \( k \) (mol/m²·s·Pa) of reaction (2) is expressed by Eq. (4)\cite{16}

\[
k = \frac{V}{ART} \ln \frac{1 - P_{eq}^1}{1 - P_{eq}^0} \quad \frac{P_{eq}^0}{P_{eq}^1} = B \quad \text{......(4)}
\]

where, \( V \) is flow rate of reaction gas \((m^3/s)\), \( A \) is the reaction area \((m^2)\), \( R \) is gas constant \((J/mol \cdot K)\), \( T \) is gas temperature \((K)\) and \( (P_{eq}^0)/P_{eq}^1 \) is partial pressure of \(^{13}\text{CO}_2\) under equilibrium of isotope exchange reaction. \( B \) is defined in Eq. (5).

\[
\frac{P_{eq}^0}{P_{eq}^1} = \frac{P_{eq}^0}{P_{eq}^1} = B \quad \text{.............(5)}
\]

### 2.2. Procedure

**Figure 1** shows the schematic cross section of reaction zone. FeO was prepared by melting a mixture of equimolar electrolytic iron and reagent grade \( \text{Fe}_2\text{O}_3\) powder in an iron crucible at \( 1\,723 \text{ K} \) in argon atmosphere for \( 30 \text{ min} \) before quenching. Prepared FeO, reagent grade of CaO, SiO\(_2\) and \( \text{Ca}_3(\text{PO}_4)_2 \) were preliminarily melted to prepare samples. About \( 5 \text{ g} \) of premelted sample were put in a platinum crucible (I.D. \( 16 \text{ mm} \), O.D. \( 23 \text{ mm} \) and height \( 18.5 \text{ mm} \)), which has the thick bottom to supply sufficient heat, and the crucible was held in an induction furnace. Temperature was measured by dual wavelength pyrometer, which was calibrated by the temperature measurement of a platinum plate heater. The gas mixtures were put in an electric furnace at \( 1\,773 \text{ K} \). The gas mixtures were prepared by mixing the high purity gases, which were passed through columns of \( \text{H}_2\text{SO}_4 \), \( \text{Mg(ClO}_4)_2 \) and, for \( \text{CO}_2 \) quenching. Prepared FeO, reagent grade of CaO, SiO\(_2\) and \( \text{Ca}_3(\text{PO}_4)_2 \) were preliminarily melted to prepare samples.

First, \( \text{CO}–^{12}\text{CO}_2 \) gas \((\text{CO} : \text{CO}_2 = 1 : 1)\) was blown into a reaction tube through the alumina tube (I.D. \( 4 \text{ mm} \)) held \( 8 \text{ mm} \) above the molten oxide surface and then crucible was heated to \( 1\,773 \pm 5 \text{ K} \). The end position of the gas inlet tube was adjusted to the center of the crucible. Sample was held for at least \( 30 \text{ min} \) to assure the equilibration with gas. Then, reaction gas was changed to \( \text{CO}–\text{CO}_2–\text{Ar} \) gas containing about \( 1\% \) of \(^{13}\text{CO}_2\) and isotope composition of outlet gas was continuously measured by quadrupole mass spectrometer. Confirming that the isotope gas composition of outlet gas became constant, isotope compositions of inlet and outlet gas were measured to calculate the reaction rate constant. After the each experiment, the oxide sample was quenched by splashing argon gas and analyzed by chemical analysis, by titration method with potassium dichromate for total iron and \( \text{Fe}_2\text{O}_3 \) analysis, by ICP-AES for calcium content, gravimetry for \( \text{SiO}_2 \) content, and molybdenum blue spectrophotometric method for phosphorus content.

### 3. Results

#### 3.1. Relationship between Rate Constant and Gas Flow Rate

In the present work, the liquid phase mass transfer does not affect the rate constant measurement theoretically. However, for the interfacial chemical reaction rate measurement, the reaction gas must be supplied sufficiently to eliminate the effect of back diffusion of inlet gas on the overall reaction rate. **Figure 2** shows the relationship between apparent rate constant and gas flow rate for \( \text{FeO} \) at \( 1\,773 \text{ K} \). The residual rate constant decreased with increasing \( \text{P}_2\text{O}_5 \) addition and the rate constant was observed at high \( \text{P}_2\text{O}_5 \) concentrations. **Figure 3** shows the effect of \( \text{P}_2\text{O}_5 \) addition on the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratios.

**Table 1** shows the dissociation rate of \( \text{CO}_2 \) on pure \( \text{FeO} \) and \( \text{Fe}_2\text{O}_3–\text{CaO} \) \((\text{mol}\%\text{Fe}_2\text{O}_3 : \text{mol}\%\text{CaO}= 6 : 4)\), \( \text{Fe}_2\text{O}–\text{SiO}_2 \) \((\text{mol}\%\text{Fe}_2\text{O} : \text{mol}\%\text{SiO}_2= 7 : 3)\) and \( \text{Fe}_2\text{O}–\text{CaO–SiO}_2 \) \((\text{mol}\%\text{Fe}_2\text{O}=35, \text{mol}\%\text{CaO} / \text{mol}\%\text{SiO}_2= 1.13–1.27 \) and \( 1.36–1.47 \) systems) are shown in Table 1 and in **Figs. 3** and 4. In each oxide system, the reaction rate constant decreased with increasing \( \text{P}_2\text{O}_5 \) addition and the residual rate constant was observed at high \( \text{P}_2\text{O}_5 \) concentrations. **Figure 5** shows the effect of \( \text{P}_2\text{O}_5 \) addition on the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratios.

Sasaki et al.\cite{31} measured the dissociation rate of \( \text{CO}_2 \) on pure \( \text{FeO} \) and \( \text{Fe}_2\text{O}_3–\text{CaO} \) melts by means of \( ^{14}\text{CO}_2–\text{CO} \) isotope exchange technique at \( 1\,693 \text{ K} \) and \( 1\,823 \text{ K} \), at the range from \( 0.38 \) to \( 12.3 \) of \( \text{CO}_2/\text{CO} \) ratio. El-Rahaiby et
Table 1. Results of reaction rates and chemical analysis for each oxide system at 1773 K.

| System                          | Exp. No. | \(P^{(1)}\text{CO}_2\) (Pa) | \(P^{(2)}\text{CO}_2\) (Pa) | \(k_\text{s} \times 10^6\) (mol/m²·s·Pa) | PO\(_{2.5}\) Content (mol%) | Fe\(^{3+}\)/Fe\(^{2+}\) ratio (--) |
|--------------------------------|----------|-----------------------------|-----------------------------|--------------------------------|-----------------------------|----------------------------------|
| **Fe\(_2\)O**                   | FP-1     | 2100                        | 1640                        | 2.131                          | 0.00                         | 0.195                            |
|                                | FP-2     | 2120                        | 1668                        | 1.999                          | 0.91                         | 0.168                            |
|                                | FP-3     | 2143                        | 1840                        | 1.197                          | 1.08                         | 0.187                            |
|                                | FP-4     | 2163                        | 1912                        | 0.956                          | 1.97                         | 0.199                            |
|                                | FP-5     | 2088                        | 1862                        | 0.869                          | 3.07                         | 0.187                            |
|                                | FP-6     | 2021                        | 1888                        | 0.514                          | 5.03                         | 0.189                            |
| **Fe\(_2\)O–CaO**              | FCP-1    | 1099                        | 837                         | 4.528                          | 0.03                         | 0.400                            |
|                                | FCP-2    | 1107                        | 867                         | 3.979                          | 0.88                         | 0.374                            |
|                                | FCP-3    | 2111                        | 1636                        | 2.144                          | 1.35                         | 0.463                            |
|                                | FCP-4    | 1111                        | 1024                        | 1.186                          | 1.81                         | 0.370                            |
|                                | FCP-5    | 1120                        | 1004                        | 1.609                          | 1.68                         | 0.405                            |
|                                | FCP-6    | 2118                        | 1841                        | 1.080                          | 2.52                         | 0.394                            |
|                                | FCP-7    | 2184                        | 1930                        | 0.949                          | 4.64                         | 0.576                            |
|                                | FCP-8    | 2080                        | 1835                        | 0.984                          | 5.03                         | 0.650                            |
| **Fe\(_2\)O–SiO\(_2\)**       | FSP-1    | 1010                        | 977                         | 0.771                          | 0.00                         | 0.092                            |
|                                | FSP-2    | 2155                        | 1990                        | 0.608                          | 0.28                         | 0.104                            |
|                                | FSP-3    | 2049                        | 1932                        | 0.443                          | 1.28                         | 0.039                            |
|                                | FSP-4    | 2113                        | 2011                        | 0.366                          | 2.51                         | 0.062                            |
|                                | FSP-5    | 2099                        | 2017                        | 0.297                          | 3.58                         | 0.054                            |
|                                | FSP-6    | 2083                        | 1992                        | 0.330                          | 4.56                         | 0.065                            |
| **Fe\(_2\)O–CaO–SiO\(_2\)**   | FCSP-1   | 601                         | 576                         | 1.034                          | 0.00                         | 0.158                            |
| (CaO/SiO\(_2\)=1.13–1.27)      | FCSP-2   | 711                         | 688                         | 0.792                          | 0.61                         | 0.158                            |
|                                | FCSP-3   | 2059                        | 1884                        | 0.665                          | 1.24                         | 0.119                            |
|                                | FCSP-4   | 1866                        | 1691                        | 0.734                          | 1.45                         | 0.173                            |
|                                | FCSP-5   | 958                         | 940                         | 0.426                          | 1.83                         | 0.126                            |
|                                | FCSP-6   | 2005                        | 1892                        | 0.440                          | 2.57                         | 0.097                            |
|                                | FCSP-7   | 843                         | 839                         | 0.117                          | 3.56                         | 0.222                            |
|                                | FCSP-8   | 1013                        | 1000                        | 0.280                          | 5.40                         | 0.366                            |
|                                | FCSP-9   | 1051                        | 1043                        | 0.167                          | 5.52                         | 0.270                            |
| **Fe\(_2\)O–CaO–SiO\(_2\)**   | FCSP-2   | 980                         | 945                         | 0.863                          | 0.00                         | 0.207                            |
| (CaO/SiO\(_2\)=1.36–1.47)      | FCSP-2   | 1003                        | 960                         | 1.021                          | 0.32                         | 0.225                            |
|                                | FCSP-3   | 929                         | 902                         | 0.691                          | 1.14                         | 0.165                            |
|                                | FCSP-4   | 1111                        | 1087                        | 0.519                          | 2.70                         | 0.216                            |
|                                | FCSP-5   | 967                         | 948                         | 0.458                          | 3.69                         | 0.180                            |
|                                | FCSP-6   | 2065                        | 1963                        | 0.417                          | 4.02                         | 0.119                            |
|                                | FCSP-7   | 933                         | 909                         | 0.615                          | 4.49                         | 0.256                            |

Fig. 3. Effect of P\(_{2}\)O\(_5\) addition on the apparent rate constant for the Fe\(_2\)O and Fe\(_2\)O–CaO systems with P\(_{CO_2}/P_{CO}\)=1 at 1773 K.

Fig. 4. Effect of P\(_{2}\)O\(_5\) addition on the apparent rate constant for the Fe\(_2\)O–SiO\(_2\) and Fe\(_2\)O–CaO–SiO\(_2\) systems with P\(_{CO_2}/P_{CO}\)=1 at 1773 K.
al.\(^7\) also measured on Fe\(_2\)O–SiO\(_2\), MnO–SiO\(_2\)\(_{\text{sat}}\) and Fe\(_2\)O–CaO–SiO\(_2\) of equimolar of CaO and SiO\(_2\). Mori et al.\(^{13}\) measured the dissociation rate on the CaO–SiO\(_2\), CaO–Al\(_2\)O\(_3\), CaO–SiO\(_2\)–CaF\(_2\) and Fe\(_2\)O–CaO–SiO\(_2\) melts by using \(^1\)CO\(_2\)–CO. Their results are shown in Figs. 3 and 4. They are in good agreement with present results.

Nagasaka et al.\(^{11}\) measured the dissociation rate on the Fe\(_3\)O–P\(_2\)O\(_5\) melt at 1 673 K by thermogravimetric method. Sun et al.\(^{12}\) measured the dissociation rate of CO\(_2\) on the melt of Fe\(_3\)O–P\(_2\)O\(_5\) melt using three types of containment tube at 1 673 K. They concluded that the use of narrow-bore containment tube causes the increase of reaction rate constant due to the hemispheric shape of surface of melt. Therefore, all data are shown in Fig. 3 except the results with narrow-bore tube. Their results have the same tendency and present result also shows the same trend. The difference of reaction rate constants seems to be due to the difference of experimental temperature.

As shown in Fig. 5, no change of the Fe\(^{3+} / \text{Fe}^{2+}\) ratio of oxides for the Fe\(_2\)O, Fe\(_2\)O–SiO\(_2\) and Fe\(_2\)O–CaO–SiO\(_2\) (CaO/SiO\(_2\)=1.36–1.47) systems was observed, and the Fe\(^{3+} / \text{Fe}^{2+}\) ratio of oxides for the Fe\(_2\)O–CaO and Fe\(_2\)O–CaO–SiO\(_2\) (CaO/SiO\(_2\)=1.13–1.27) systems was slightly increased.

From comparison of rate constants for each oxide system at 0 mol% PO\(_2\)\(_{0.5}\), it is obvious that the increasing the Fe\(^{3+} / \text{Fe}^{2+}\) ratio increases the reaction rate constant \(k_8\) at \(P_{\text{CO}_2}/P_{\text{CO}}\), ratio of unity. Belton group\(^{17,18}\) investigated the effect of CaO or SiO\(_2\) addition on the dissociation rate of CO\(_2\) on the Fe\(_2\)O-rich melts at 1 573 to 1 793 K, and they also found the same trend. In the present work, the effective change of Fe\(^{3+} / \text{Fe}^{2+}\) ratio was not observed as shown in Fig. 5. Nevertheless, the addition of P\(_2\)O\(_5\) decreased the reaction rate constant as shown in Figs. 3 and 4. Therefore, the strong surface active effect of P\(_2\)O\(_5\) in molten oxide strongly affects the reaction rate of CO\(_2\) dissociation on molten oxide for each melt.

### 4. Discussion

#### 4.1. Estimation of the Effect of Gas Phase Mass Transfer on the Rate Constant

For estimation of the interfacial chemical reaction rate constant, \(k_a\), from measured rate constant \(k_c\), effect of gas phase mass transfer is estimated. The relationship between the apparent rate constant, the gas phase mass transfer coefficient and the chemical reaction rate constant is expressed as follows,

\[
\frac{1}{k_c} + \frac{1}{k_g/RT} = \frac{1}{k_a} \quad \text{..........................}(6)
\]

Taniguchi et al.\(^{17}\) measured the oxidation rate of graphite put in a crucible-type reactor (I.D. 38 mm) by flowing CO–CO\(_2\) gas, and proposed Eq. (7) from their results,

\[
Sh = n \left( \frac{r_g}{d} \right)^{-1.5} Re^{0.66} Sc^{0.5} \quad \text{..........................}(7)
\]

where, \(n\) is a constant deduced from their experiments (=0.32±0.06). The present study was done by the approximately same size with their work, therefore Eq. (7) is applicable for estimation of gas phase mass transfer coefficient of the present work. The viscosity and diffusion coefficient of gas were calculated by Chapman-Enskog equations.\(^{18}\) The estimated \(Re\), \(Sc\) and \(k_g/RT\), and calculated interfacial chemical reaction rate constants \(k_a\) are summarized in Table 2 and shown in Figs. 6 and 7 as a function of mol% PO\(_2\)\(_{0.5}\). Experiments with the Fe\(_3\)O–P\(_2\)O\(_5\) system were conducted with gas flow rates of approximately 3.3×10^{-6} m\(^3\)/s STP, therefore observed rate constants would be affected by both of interfacial reaction rate and the gas phase mass transfer.

#### 4.2. Discussion of the Rate Controlling Step of CO\(_2\) Dissociation

Strong blocking effect of P\(_2\)O\(_5\) on CO\(_2\) dissociation was observed as shown in Figs. 6 and 7. Therefore, disturbing effect by P\(_2\)O\(_5\) addition on the CO\(_2\) dissociation was analyzed by using “site blockage model” that phosphorus oxide occupies CO\(_2\) reaction sites on the molten oxides. Assuming the ideal Langmuir adsorption isotherm, Eq. (8) is obtained,

\[
K_F = \frac{\theta_p}{a_{P_{O_2}} (1-\theta_p)} \quad \text{.....................}(8)
\]

Equation (8) indicates that when the concentration of P\(_2\)O\(_5\) becomes high, the surface coverage \(\theta_p\) almost keeps constant, therefore this Langmuir adsorption isotherm would be applicable for the analysis of the present results which show the residual rate constants at high P\(_2\)O\(_5\) concentration region over approximately 3 mol% P\(_2\)O\(_5\).

When the surface active element such as P\(_2\)O\(_5\) or Na\(_2\)O is contained on the surface like the present investigation, the measured constant is expressed as a function of surface coverage with surfactants, and the dependency is different on the rate determining step of the observed reaction.

Two steps are considered as the rate controlling step of
CO₂ dissociation. One is the adsorption reaction of CO₂ molecule expressed as CO₂(g)→CO₂(ad), and the other is the dissociation reaction of adsorbed CO₂ molecule expressed as CO₂(ad)→CO(ad) + O(ad).

(1) The Adsorption Reaction as the Rate Controlling Step

Assuming the rate controlling step is the adsorption reaction, Eq. (9) is obtained,

\[ k_c = k_0(1 - \theta) + k_1 \theta \]  

where, \( k_0 \) and \( k_1 \) are the rate constants of CO₂ adsorption at

Table 2. Estimated results of interfacial reaction rate constant.

| System               | Exp. No. | Re  | Sc  | \( k_c/RT \times 10^6 \) (mol/m²·s·Pa) | \( k_c \times 10^6 \) (mol/m²·s·Pa) |
|----------------------|----------|-----|-----|--------------------------------------|-----------------------------------|
| Fe₂O                | FP-1     | 26.7| 0.803 | 4.90 | 3.770 |
|                     | FP-2     | 25.9| 0.799 | 4.79 | 3.430 |
|                     | FP-3     | 26.0| 0.800 | 4.81 | 1.593 |
|                     | FP-4     | 26.1| 0.798 | 4.81 | 1.194 |
|                     | FP-5     | 25.7| 0.803 | 4.77 | 1.063 |
|                     | FP-6     | 26.1| 0.802 | 4.82 | 0.576 |
| Fe₂O-CaO            | FCP-1    | 45.7| 0.835 | 7.53 | 11.347 |
|                     | FCP-2    | 45.6| 0.835 | 7.52 | 8.446 |
|                     | FCP-3    | 25.8| 0.802 | 4.79 | 3.880 |
|                     | FCP-4    | 45.6| 0.835 | 7.52 | 1.408 |
|                     | FCP-5    | 45.7| 0.835 | 7.53 | 2.046 |
|                     | FCP-6    | 25.8| 0.802 | 4.79 | 1.395 |
|                     | FCP-7    | 25.9| 0.796 | 4.78 | 1.184 |
|                     | FCP-8    | 26.5| 0.797 | 4.86 | 1.234 |
| Fe₂O-SiO₂           | FSP-1    | 73.3| 0.846 | 10.54 | 0.832 |
|                     | FSP-2    | 26.4| 0.799 | 4.86 | 0.694 |
|                     | FSP-3    | 26.3| 0.804 | 4.85 | 0.487 |
|                     | FSP-4    | 26.1| 0.802 | 4.82 | 0.396 |
|                     | FSP-5    | 26.4| 0.799 | 4.86 | 0.317 |
|                     | FSP-6    | 25.9| 0.799 | 4.79 | 0.354 |
| Fe₂O-CaO-SiO₂       | FCSPI-1  | 77.5| 0.847 | 10.99 | 1.142 |
|                     | FCSPI-2  | 76.0| 0.845 | 10.81 | 0.854 |
|                     | FCSPI-3  | 25.7| 0.800 | 4.78 | 0.772 |
|                     | FCSPI-4  | 25.2| 0.818 | 4.76 | 0.687 |
|                     | FCSPI-5  | 72.1| 0.848 | 10.48 | 0.444 |
|                     | FCSPI-6  | 26.5| 0.803 | 4.87 | 0.484 |
|                     | FCSPI-7  | 72.4| 0.848 | 10.52 | 0.119 |
|                     | FCSPI-8  | 73.1| 0.848 | 10.57 | 0.288 |
|                     | FCSPI-9  | 73.9| 0.844 | 10.59 | 0.169 |
| Fe₂O-CaO-SiO₂ (CaO/SiO₂=1.13–1.27) | FCSPI-1 | 74.6| 0.846 | 10.66 | 0.939 |
|                     | FCSPI-2  | 74.8| 0.846 | 10.45 | 1.132 |
|                     | FCSPI-3  | 72.5| 0.848 | 10.47 | 0.740 |
|                     | FCSPI-4  | 75.6| 0.848 | 10.76 | 0.545 |
|                     | FCSPI-5  | 74.6| 0.845 | 10.61 | 0.478 |
|                     | FCSPI-6  | 26.5| 0.796 | 4.84 | 0.457 |
|                     | FCSPI-7  | 74.4| 0.848 | 10.67 | 0.652 |

Fig. 6. Relationship between estimated interfacial chemical reaction rate constant \( k_c \) and PO₂ content for the Fe₂O and Fe₂O-CaO systems with \( P_{CO}/P_{CO} \)=1 at 1773 K.

Fig. 7. Relationship between estimated interfacial chemical reaction rate constant \( k_c \) and PO₂ content for the Fe₂O–SiO₂ and Fe₂O–CaO–SiO₂ systems with \( P_{CO}/P_{CO} \)=1 at 1773 K.
the free site and at the occupied site, respectively. As above mentioned, even at the high concentration region the residual rate constants were observed. This is considered as the indication that the isotope exchange reaction occurs at the occupied sites by phosphorus oxide. The residual rate constant is also observed with the addition of some elements for the dissolution of nitrogen gas into molten iron.19–23)

From Eqs. (8) and (9), Eq. (10) is obtained,

\[
\frac{1}{k_e - k_0} = \frac{1}{k_1 - k_0} + \frac{1}{k_0' (k_1 - k_0)} (\text{mol}\% \text{PO}_{2.5}) \tag{10}
\]

where, \(K'_p\) is defined as \(k_p' \times \gamma_{\text{PO}_{2.5}}\).

**Figure 8** shows the relationship between P\(_2\)O\(_5\) content and the rate constant according to Eq. (10).

(2) The Dissociation Reaction as the Rate Controlling Step

On the other hand, when assuming the rate controlling step is the dissociation reaction of adsorbed CO\(_2\) molecule, the reaction rate is expressed as follows,

\[
r = k_1 a_{\text{CO}_2,\text{ad}} (1 - \theta_p) - k_2 a_{\text{CO}_2,\text{ad}} a_{\text{O}_2,\text{ad}} \tag{11}
\]

Here, the adsorption reactions of CO\(_2\), CO and O\(_2\) are assumed to be in equilibrium, therefore three equations are deduced as follows,

\[
K_{\text{CO}_2} = \frac{a_{\text{CO}_2,\text{ad}}}{P_{\text{CO}_2} (1 - \theta_p)} \tag{12}
\]

\[
K_{\text{CO}} = \frac{a_{\text{O}_2,\text{ad}}}{P_{\text{CO}} (1 - \theta_p)} \tag{13}
\]

\[
K_{\text{O}_2} = \frac{a_{\text{O}_2,\text{ad}}}{P_{\text{O}_2}^{1/2} (1 - \theta_p)} \tag{14}
\]

and CO–CO\(_2\) reaction is also assumed to be in equilibrium, therefore Eq. (15) is obtained,

\[
K_{\text{CO}-\text{CO}_2} = \frac{P_{\text{CO}}}{P_{\text{CO}} P_{\text{O}_2}^{1/2}} \tag{15}
\]

Using Eqs. (12)–(15), Eq. (11) is transformed into Eq. (16).

\[
r = k_1 K_{\text{CO}_2} - k_2 K_{\text{CO}} K_{\text{O}_2} (1 - \theta_p)^2 P_{\text{CO}_2} = k_0 (1 - \theta_p)^2 P_{\text{CO}_2} = k_0' P_{\text{CO}_2} \tag{16}
\]

By using Eq. (8), finally the following relationship is deduced,

\[
\frac{1}{\sqrt{k_e}} = \frac{K_p'}{\sqrt{k_0'}} (\text{mol}\% \text{PO}_{2.5}) + \frac{1}{\sqrt{k_0'}} \tag{17}
\]

**Figure 9** shows the relationship between P\(_2\)O\(_5\) content and the rate constant according to Eq. (17).

Comparing results analyzed by two assumptions, a good linear relationship was observed in Fig. 9. Therefore, the dissociation reaction of adsorbed CO\(_2\) molecule on the surface of molten oxide seems to be the rate controlling step of reaction (1). It will be needed to consider the reaction including electron(s) to clarify the more detail of reaction, however in the present study, the effect of Fe\(^{3+}/\text{Fe}^{2+}\) ratio on the reaction rate constant was not investigated. Belton group\(^{3,7,8,12}\) investigated the effect Fe\(^{3+}/\text{Fe}^{2+}\) on the rate constant and concluded the rate-determining step of the reaction is expressed as follows\(^{12}\),

\[
\text{CO}_2(\text{ad}) + 2e^- = \text{O}_2(\text{ad}) + \text{CO}(\text{ad}) \tag{18}
\]

and the present result follows their conclusion.

5. Conclusions

The effect of P\(_2\)O\(_5\) addition on the reaction rate of CO\(_2\) dissociation on the surface of FeO–base molten oxides was investigated by using isotope exchange technique at 1773 K and the following results were obtained.

(1) The rate constant decreased with increasing P\(_2\)O\(_5\) content and the residual rate constant was observed at high P\(_2\)O\(_5\) content, though the change of the Fe\(^{3+}/\text{Fe}^{2+}\) ratio of oxides was not observed.
(2) The rate controlling step of $^{13}$CO$_2$ + $^{12}$CO = $^{13}$CO + $^{12}$CO$_2$ was the dissociation reaction of adsorbed CO$_2$ molecule on the surface of molten oxide expressed as

$$\text{CO}_2(\text{ad}) = \text{CO}(\text{ad}) + \text{O(}\text{ad})$$

from the analysis by using site blockage model by phosphorus oxide, and the relationship between reaction rate constant and P$_2$O$_5$ content in melts is represented as

$$\frac{1}{\sqrt{k_c}} = \frac{K_P}{k_0}(\text{mol}\% \text{PO}_{2.5}) + \frac{1}{\sqrt{k_0}}$$

where, $K_P$ is the adsorption coefficient of P$_2$O$_5$ including the activity coefficient $\gamma_{\text{PO}_{2.5}}$.

**Nomenclature**

- $a_A$: Activity of species A
- $A$: Reaction area
- $d$: Inner diameter of inlet gas nozzle
- $D$: Diffusion coefficient in gas phase
- $k_0, k_1$: The rate constants of CO$_2$ adsorption on the free site and on the occupied site
- $k_e$: Apparent reaction rate constant
- $k$: The interfacial chemical reaction rate constant
- $k_i, k_f$: The rate constants of forward and inverse reaction of CO$_2$ dissociation
- $k_g$: The gas phase mass transfer coefficient
- $K_A$: Equilibrium constant for the reaction of species A
- $K_P$: The adsorption coefficient for PO$_{2.5}$
- $P_{\text{inlet}}, P_{\text{outlet}}$: Partial pressures of $^{13}$CO$_2$ in inlet and outlet gas
- $(P_{\text{inlet}})_{\text{eq}}$: Partial pressure of $^{13}$CO$_2$ under the equilibration of reaction (1)
- $R$: Gas constant
- $Re$: Reynolds number ($=dup/\mu$)
- $Sc$: Schmidt number ($=\mu/\rho D$)
- $Sh$: Sherwood number ($=k_g d/D$)
- $r_s$: Sample radius
- $T$: Gas temperature
- $u$: Linear velocity of jet gas
- $V$: Volumetric flow rate of reaction gas

$\gamma_A$: Activity coefficient of species A

$\theta_p$: The fraction of CO$_2$ reaction sites occupied by PO$_{2.5}$

$\mu$: Viscosity of reaction gas

$\rho$: Density of reaction gas

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