Surface Active Effect of Na$_2$O on the Rate of CO$_2$ Dissociation on the Surface of Molten FeO$_x$–Na$_2$O and FeO$_x$–SiO$_2$–Na$_2$O Systems

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It is well known that P$_2$O$_5$ and Na$_2$O have strong surface active effect in the molten oxide systems and affect the rate of oxidation or reduction of melts. In the previous work, the effect of P$_2$O$_5$ addition on the rate of CO$_2$ dissociation on the surface of FeO$_x$ (FeO and Fe$_2$O$_3$)-based molten oxides was investigated by isotope exchange technique and it was confirmed that P$_2$O$_5$ strongly disturbs CO$_2$ dissociation. In the present study, the effect of Na$_2$O addition on the rate of CO$_2$ dissociation on the surface of FeO$_x$–Na$_2$O and FeO$_x$–SiO$_2$–Na$_2$O (mol%FeO$_x$: mol%SiO$_2$=65:35) melts was measured at 1773 K with P$_{CO_2}$/P$_{CO}$=1 by isotope exchange technique. Reaction rate constant drastically increased with increasing Na$_2$O content for the FeO$_x$–Na$_2$O system. On the other hand, rate constant gently increased for the FeO$_x$–SiO$_2$–Na$_2$O system. The Fe$^{3+}$/Fe$^{2+}$ ratio of each system also slightly increased.

To estimate the rate constant from the composition of melts, the relationship between the rate constant and the Fe$^{3+}$/Fe$^{2+}$ ratio for the FeO$_x$–CaO–SiO$_2$ system was also investigated. From the comparison of the estimated and observed rate constants, the strong promoting effect of Na$_2$O for CO$_2$ dissociation was confirmed in the FeO$_x$–Na$_2$O system.

The surface active effect of Na$_2$O was analyzed by "smoothed surface potential model", and the nature of molten oxide was discussed. From the obtained values, the surface tension of the molten oxide was estimated as a function of Na$_2$O concentration.

KEY WORDS: kinetics; reaction mechanism; isotope exchange technique; molten oxide; Na$_2$O; surface active effect; smoothed surface potential model; surface tension.

1. Introduction

The reactions between CO–CO$_2$ gas and FeO$_x$-based molten oxides are quite important and the main phenomena in ironmaking and steelmaking processes. Therefore, oxidation or reduction rates for FeO$_x$-containing oxides have been widely investigated.1–13) Researches about the reduction rate of FeO$_x$ and Fe$_2$O$_3$-based molten oxides with CO–CO$_2$ gas have been conducted by many researchers. Tsukihashi et al.2) measured the reduction rate of molten iron oxide in CO gas conveyed system at 1723 and 1873 K. Fine powders of iron oxide were utilized to eliminate the effect of gas phase mass transfer rate on the overall reaction rate of reduction. Nagasaka et al.9) also measured the reduction rate of molten iron oxide contained in an iron crucible under strong CO gas flow by using thermobalance in the temperature range of 1673 to 1723 K. Measured reduction rate constants were quite in good agreement with those measured by Tsukihashi et al. Meanwhile, the dissociation rates of CO$_2$ on the surface of molten oxides containing iron oxide have been measured by Sasaki et al.,3) El-Rahayib et al.,7) Sun et al.8) and Mori et al.11) with isotope exchange technique. If the dissociation of CO$_2$ is the rate determining step of oxidation of molten oxide, the reduction rate could be calculated from the measured dissociation rate constant. Belton14) reported that there is very good accordance between the measured reduction rate and the dissociation rate. Therefore, the dissociation reaction of CO$_2$ is strongly expected as the rate determining step of the reaction between CO–CO$_2$ gas and molten oxide. Nagasaka et al.5,10) estimated the dissociation rate constants of CO$_2$ from their measured reduction rate constant and those values were identical with measured values with isotope exchange technique.

Nagasaka et al.10) also measured the effect of additives on the reduction rate of Fe$_2$O$_3$-based molten oxide and it has been confirmed that the reaction rate constants are expressed as functions of temperature and compositions of ferrous and ferric iron in the molten oxides which represent thermodynamic state of melts. However, this expression could not be applied for molten oxides containing P$_2$O$_5$ or Na$_2$O due to their strong surface active effect.

The effect of Na$_2$O addition on the reaction rates has been investigated by Nagasaka et al.10) and Sun and Belton.12) Nagasaka et al. investigated the effect of Na$_2$O addition on the reduction rate of molten iron oxide with CO gas gravimetrically and the reduction rate constant increased 1.5 times by the approximately 4 mass% of Na$_2$O.
addition. Sun and Belton measured the dissociation rate of \( \text{CO}_2 \) on the molten \( \text{FeO} - \text{Na}_2\text{O} \) at 1 673 K with \( \text{CO}_2/\text{CO} = 5 \) by \( ^{13}\text{CO}_2 - \text{CO} \) isotope exchange technique, and they qualitatively confirmed the increase of dissociation rate constant by the small addition of \( \text{Na}_2\text{O} \). However, the correct and quantitative analysis of the effect of \( \text{Na}_2\text{O} \) addition could not be conducted because of the inaccurate measured data due to the high volatility of \( \text{Na}_2\text{O} \).

Therefore, available data are limited for the evaluation of the surface active effect of \( \text{Na}_2\text{O} \) on the reaction rate constant and for discussion of reaction mechanism. From this point of view, in the present study, the effect of \( \text{Na}_2\text{O} \) addition on the dissociation rate constant of \( \text{CO}_2 \) on the surface of the \( \text{FeO} - \text{Na}_2\text{O} \) and the \( \text{FeO} - \text{SiO}_2 - \text{Na}_2\text{O} \) systems has been investigated by using \( ^{13}\text{CO}_2 - \text{CO} \) isotope exchange technique\(^{15} \) at 1 773 K to confirm the surface active effect of \( \text{Na}_2\text{O} \) and to clarify the applicability of surface covering model for the explanation of observed phenomena. The effect of \( \text{Na}_2\text{O} \) addition and the reaction mechanism were discussed based on the comparison with the effect of \( \text{P}_2\text{O}_5 \) addition previously investigated by present authors at 1 773 K.\(^{16} \)

2. Experimental

In the present study, \( \text{CO} - \text{CO}_2 \) gas containing \( ^{13}\text{CO}_2 \) was utilized. Therefore, the isotope exchange reaction expressed as Eq. (1) occurs on the surface of molten oxide,

\[
^{13}\text{CO}_2 + ^{12}\text{CO} = ^{13}\text{CO} + ^{12}\text{CO}_2
\]

and the forward reaction rate constant of Eq. (1) is expressed as Eq. (2),\(^{14} \)

\[
k = \frac{V}{ART} \left[ \frac{1}{B+1} \ln \left( \frac{P_{\text{CO}_2}^i / \langle P_{\text{CO}_2} \rangle_{eq}}{1 - P_{\text{CO}_2}^i / \langle P_{\text{CO}_2} \rangle_{eq}} \right) \right]_{eq} \quad (2)
\]

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

\[
\frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \left( \frac{P_{\text{CO}_2} / P_{\text{CO}}} \right)_{eq} = B \quad (3)
\]

The detail of experimental apparatus and procedures were essentially the same as reported in the previous paper.\(^{16} \) About 5 g of premelted sample was put in a platinum crucible (I.D. 16 mm, O.D. 23 mm and height 18.5 mm), which has a thick bottom to supply sufficient heat, and that crucible and alumina tube (I.D. 16 mm, O.D. 21 mm and length 200 mm) were inserted in a transparent quartz tube (I.D. 45 mm, O.D. 50 mm and length 400 mm) which was set in an induction furnace. Sun and Belton\(^{12} \) used about 0.5 g of slag films for their experiments, however \( \text{Na}_2\text{O} \) content of slag was drastically decreased due to the high volatility of \( \text{Na}_2\text{O} \) and correct measurements were inhibited. To avoid this problem, slag volumes used in the present study were increased to about 5 g and the effect of \( \text{Na}_2\text{O} \) content was successfully measured. As \( \text{Na}_2\text{O} \) content of slag decreased by volatilization, final \( \text{Na}_2\text{O} \) composition was determined by chemical analysis. Crucible and alumina tube were connected carefully and tightly to prevent the reaction gas from contacting platinum which has high catalysis for isotope exchange reaction. Temperature was measured by dual wavelength pyrometer, which was calibrated by the temperature measurement of a platinum plate put in an electric furnace at 1 773 K.

\( \text{FeO} \) 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 K in argon atmosphere for 30 min before quenching on a steel plate. Prepared \( \text{FeO} \), reagent grade of \( \text{SiO}_2 \) and \( \text{Na}_2\text{CO}_3 \) were preliminarily melted to prepare samples. 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 \( \text{CO} \) gas, soda lime for purification.

First, \( \text{CO} - ^{12}\text{CO}_2 \) gas (\( \text{CO}_2/\text{CO} = 1 \)) was blown into a reaction tube through an alumina tube (I.D. 4 mm and O.D. 6 mm) held 8 mm above the surface of sample, and then crucible was heated to 1 773 ± 5 K. The end position of the gas inlet tube was adjusted to the center of the crucible. Sample was held for at least 30 min to assure the equilibration with gas. Then, reaction gas was changed to \( \text{CO} - \text{CO}_2 - \text{Ar} \) gas containing about 2% of \( ^{13}\text{CO}_2 \) with flow rate of approximately 5 × 10\(^{-4} \) m\(^3\)/s STP and isotope composition of outlet gas was continuously measured by quadrupole mass spectrometer (QMS). Confirming that the isotope gas composition of outlet gas became constant, isotope compositions of inlet and outlet gas were measured. After the each experiment, the oxide sample was quenched by splashing argon gas and analyzed by titration method with potassium dichromate for total iron and \( \text{Fe}^{2+} \) contents, ICP-AES for sodium content and gravimetry for \( \text{SiO}_2 \) content, respectively.

3. Results

Figure 1 shows an example of ion current profiles for each gas species measured by QMS. From these average ion currents of each species, \( P_{\text{CO}_2}/P_{\text{CO}} \) and \( P_{\text{CO}_2}/P_{\text{CO}_2} \) were calculated for the following calculation of reaction rate constant.

Experimental results and observed reaction rate constants at 1 773 K for the \( \text{FeO}_2 - \text{Na}_2\text{O} \) and the \( \text{FeO}_2 - \text{SiO}_2 - \text{Na}_2\text{O} \) systems are listed in Table 1.
Table 1. Results of measured reaction rates and chemical analysis for each oxide system.

| System                | Exp. No. | $P^{(13)CO_2}$/Pa | $P^{(13)CO_2}$/Pa | $k_x \times 10^6$ (mol/m²·s·Pa) | NaO_{0.5} content (mol%) | Fe^{3+}/Fe^{2+} ratio (-) |
|-----------------------|----------|-------------------|-------------------|---------------------------------|--------------------------|---------------------------|
| FeO$_x$-Na$_2$O        | FN-1     | 753               | 653               | 3.681                           | 0.00                     | 0.177                     |
|                       | FN-2     | 857               | 743               | 3.372                           | 0.00                     | 0.192                     |
|                       | FN-3     | 803               | 659               | 5.178                           | 0.83                     | 0.215                     |
|                       | FN-4     | 772               | 599               | 6.711                           | 2.08                     | 0.199                     |
|                       | FN-5     | 765               | 592               | 7.542                           | 2.42                     | 0.192                     |
|                       | FN-6     | 861               | 645               | 8.147                           | 3.59                     | 0.225                     |
|                       | FN-7     | 774               | 535               | 11.457                          | 7.45                     | 0.238                     |
|                       | FN-8     | 756               | 510               | 13.343                          | 9.74                     | 0.259                     |
|                       | FN-9     | 751               | 519               | 14.060                          | 12.84                    | 0.249                     |
|                       | FN-10    | 685               | 509               | 14.889                          | 15.82                    | 0.280                     |
| FeO$_x$-SiO$_2$-Na$_2$O | FSN-1    | 820               | 800               | 0.543                           | 0.00                     | 0.130                     |
|                       | FSN-2    | 853               | 843               | 0.288                           | 1.19                     | 0.104                     |
|                       | FSN-3    | 859               | 847               | 0.339                           | 2.67                     | 0.073                     |
|                       | FSN-4    | 848               | 829               | 0.554                           | 3.13                     | 0.079                     |
|                       | FSN-5    | 849               | 829               | 0.569                           | 6.65                     | 0.109                     |
|                       | FSN-6    | 559               | 548               | 0.468                           | 12.07                    | 0.154                     |
|                       | FSN-7    | 772               | 752               | 0.631                           | 12.78                    | 0.135                     |
|                       | FSN-8    | 921               | 900               | 0.544                           | 15.07                    | 0.152                     |
|                       | FSN-9    | 845               | 811               | 0.989                           | 16.92                    | 0.125                     |
|                       | FSN-10   | 844               | 814               | 0.863                           | 19.35                    | 0.151                     |
|                       | FSN-11   | 838               | 803               | 1.022                           | 21.71                    | 0.128                     |
|                       | FSN-12   | 846               | 813               | 1.009                           | 21.97                    | 0.218                     |

In the case of experiments containing high concentration of Na$_2$O, the gas phase mass transfer might affect the measurements of reaction rate constants. Therefore, for FeO$_x$-Na$_2$O containing 12.8 mol% and 15.8 mol% NaO$_{0.5}$ systems, the experiments were conducted with high gas flow rate, which is approximately twice (1×10$^{-5}$ m$^3$/s STP). Nevertheless, the measured results showed the same trend as the results with normal gas flow rate, which indicates, in the present experimental conditions, the effect of gas phase mass transfer is negligibly small even with the high reaction rate constants. From this finding, all results were analyzed with the assumption that measured reaction rate constants are equivalent to the interfacial reaction rate constants.

Nagasaka et al. investigated the effect of Na$_2$O addition on the reduction rate of FeO in FeO–Na$_2$O melts with
CO gas at 1673 K by thermogravimetric method. Their results were converted into the rate constants at 1773 K by using the activation energy of 138 kJ/mol\(^{10}\) and are plotted in Fig. 2, which also show the increase of rate constant by the addition on Na\(_2\)O. Larger increase with Na\(_2\)O addition was observed in the present experiments. Sun and Belton\(^{12}\) measured the dissociation rate of CO\(_2\) on the molten FeO\(_x\)–Na\(_2\)O at 1673 K with CO\(_2\)/CO\(_1\)=5 and their measured data are also shown in Fig. 2. Their experiments were conducted for about 10 to 23 min to collect outlet gases for analyses of \(^{14}\)CO content produced by the isotope exchange reaction. However, due to the high volatility of sodium oxide and the small slag amount of about 0.5 g, Na\(_2\)O content of slag was drastically decreased as mentioned above. Therefore, Na\(_2\)O content of samples were considered to change during experiments and the relationship between reaction rate constant and the Na\(_2\)O content could not be clearly derived.

To clarify the change of the reaction rate constant with the Fe\(^{3+}/\)Fe\(^{2+}\) ratio of molten oxides, some experiments were conducted for the FeO\(_x\)–CaO–SiO\(_2\) system with CO\(_2\)/CO\(_1\)=1. Relationship between log (Fe\(^{3+}/\)Fe\(^{2+}\)) and log \(k\) is shown in Fig. 5 with the results observed in the previous paper.\(^{16}\) It is known that the change of log (Fe\(^{3+}/\)Fe\(^{2+}\)) by the change of CO\(_2\)/CO ratio shows the linear relationship with log \(k\) with a slope of \(-2\) for pure FeO\(_x\), FeO\(_x\)–SiO\(_2\), FeO\(_x\)–CaO\(^{13}\) and FeO\(_x\)–CaO–SiO\(_2\)\(^{17}\) melts and these results indicate that two electrons play a key role for the dissociation of CO\(_2\) on the melt. However, the change of Fe\(^{3+}/\)Fe\(^{2+}\) was observed with changing CaO/SiO\(_2\) ratio of slag system under constant CO\(_2\)/CO ratio in the present study. The reaction rate was increased by the increase of Fe\(^{3+}/\)Fe\(^{2+}\) of melts. The dotted line measured by Sasaki et al.,\(^3\) El-Rahaiby et al.,\(^7\) and Sun et al.,\(^8\) at 1793 K shows the same trend. From present results, change of reaction rate constant was expressed as a function of Fe\(^{3+}/\)Fe\(^{2+}\) ratio.

4. Discussion

4.1. Surface Active Effect of Na\(_2\)O on the Reaction Rate Constant

For both the FeO\(_x\)–Na\(_2\)O and the FeO\(_x\)–SiO\(_2\)–Na\(_2\)O systems, the Fe\(^{3+}/\)Fe\(^{2+}\) ratio was increased with increasing Na\(_2\)O content as expressed by Eqs. (4) and (5), respectively. Therefore, the change of the reaction rate constants with Na\(_2\)O addition could be estimated from the Fe\(^{3+}/\)Fe\(^{2+}\) ratio of melts by using Eqs. (4) and (5) with obtained relationship in Fig. 5. In Fig. 6, the dotted lines show the estimated reaction rate constants for both systems. For the FeO\(_x\)–Na\(_2\)O system, a large difference between measured and estimated rate constants is observed, which is considered due to the surface active effect of Na\(_2\)O. Meanwhile, for the FeO\(_x\)–SiO\(_2\)–Na\(_2\)O system, the measured and estimated constants are almost the same; this result indicates that Na\(_2\)O is not surface active for the FeO\(_x\)–SiO\(_2\)–Na\(_2\)O system under the present condition. Na\(_2\)O has strong affinity with SiO\(_2\) and the activity of Na\(_2\)O decreases with the increase of SiO\(_2\) content in the silicate melts.\(^{17}\) Therefore, it is considered that the segregation of Na\(_2\)O on the surface of melts is less activated for the FeO\(_x\)–SiO\(_2\)–Na\(_2\)O system in comparison with the FeO\(_x\)–Na\(_2\)O system because of the decrease of Na\(_2\)O activity.
4.2. Effect of Na$_2$O Addition on the Rate Constant and the Estimation of Surface Coverage

As mentioned above, Na$_2$O addition drastically increases the rate constant more than estimated from the change of the Fe$^{3+}$/Fe$^{2+}$ ratio of FeO–Na$_2$O melts. This phenomenon is considered as the surface active effect of Na$_2$O, which is known as drastic decrease of surface tension with the addition of Na$_2$O caused by the segregation of Na$_2$O for the FeO–Na$_2$O system as shown in Fig. 7.$^{18,19}$

Comparing the effect of Na$_2$O addition with that of P$_2$O$_5$ reported in the previous paper,$^{16}$ the strong promoting effect of Na$_2$O is observed, which is different from the strong disturbing effect by P$_2$O$_5$ addition. The difference is considered to be originated with the affinity of Na$_2$O or P$_2$O$_5$ and CO$_2$ molecule. However, when the nature of molten oxides is considered, the affecting mechanism for CO$_2$ dissociation might be different between P$_2$O$_5$ and Na$_2$O addition, because the addition of Na$_2$O induces the increase of the Fe$^{3+}$/Fe$^{2+}$ ratio, while the addition of P$_2$O$_5$ does not affect. In the case of P$_2$O$_5$ addition, PO$_4^{3-}$ or their polymerized anions cover the surface of melts while the surface Fe$^{3+}$/Fe$^{2+}$ ratio keeps almost constant, which simply interfere the adsorption and/or the dissociation of CO$_2$ molecule.

Recently, Sun and Belton$^{12}$ proposed “smoothed surface potential model” for the surface active effect of P$_2$O$_5$ and Na$_2$O, which explains the effect of P$_2$O$_5$ or Na$_2$O addition on the rate constant as the change of local band gap between the conduction band and the valence band at the surface due to the change of surface potential with the addition of surfactants. Based on their model, the surface activity of Na$_2$O is written as Eq. (6),

\[
\ln \frac{k}{k_0} = - \frac{2F}{RT} \Delta \Phi_{NaO_{0.5}} \theta_{NaO_{0.5}} \tag{6}
\]

where, $k$ and $k_0$ are the rate constant when surface is covered with Na$_2$O of coverage $\theta_{NaO_{0.5}}$, and that with bare surface, respectively. $F$ is Faraday constant. $\Delta \Phi_{NaO_{0.5}}$ is the change of surface potential when the surface is saturated with Na$_2$O. From above discussion, this model might be applicable to analyze the effect of Na$_2$O addition. To investigate the relationship between $\ln(k/k_0)$ and $\theta_{NaO_{0.5}}$, it is necessary to express the surface coverage with Na$_2$O as a function of Na$_2$O concentration. Applying the ideal Langmuir adsorption isotherm, surface coverage is expressed as a function of Na$_2$O content as Eq. (8),

\[
\text{NaO}_{0.5}\text{(in slag)} + \quad = \quad \text{NaO}_{0.5}\text{(ad)} \tag{7}
\]

\[
\theta_{NaO_{0.5}} = \frac{K_{NaO_{0.5}} a_{NaO_{0.5}}}{1 + K_{NaO_{0.5}} a_{NaO_{0.5}}} = \frac{K'_{NaO_{0.5}} X_{NaO_{0.5}}}{1 + K'_{NaO_{0.5}} X_{NaO_{0.5}}} \tag{8}
\]

where, $K_{NaO_{0.5}}$, $a_{NaO_{0.5}}$, and $X_{NaO_{0.5}}$ are the adsorption coefficient of Eq. (7), activity and mole fraction of NaO$_{0.5}$, respectively. The standard state of activity is pure liquid of Na$_2$O. $K'_{NaO_{0.5}}$ is defined as $K'_{NaO_{0.5}} = K_{NaO_{0.5}} X_{NaO_{0.5}}$. Therefore, by combining Eqs. (6) and (8), the following relationship is deduced,

\[
\ln \frac{k}{k_0} = - \frac{2F}{RT} \Delta \Phi_{NaO_{0.5}} \times \frac{K'_{NaO_{0.5}} X_{NaO_{0.5}}}{1 + K'_{NaO_{0.5}} X_{NaO_{0.5}}} \tag{9}
\]

As shown in Fig. 8, the fitting curve shows extremely good agreement with present results.

From obtained $K_{NaO_{0.5}}$, it is possible to estimate the surface tension of the FeO–Na$_2$O melt by the use of Langmuir-Szyszkowski equation, which was derived by Belton$^{20}$ from the combination of Langmuir adsorption isotherm and Gibbs adsorption isotherm as Eq. (11),

\[
\sigma = \sigma^0 - RT \Gamma_{NaO_{0.5}}^\text{sat} \ln(1 + K_{NaO_{0.5}} a_{NaO_{0.5}}) = \sigma^0 - RT \Gamma_{NaO_{0.5}}^\text{sat} \ln(1 + K'_{NaO_{0.5}} X_{NaO_{0.5}}) \tag{11}
\]
where, $\sigma$ and $\Gamma_{\text{Na}_2\text{O}}^{\text{sat}}$ are the surface tension of pure FeO and the saturating surface concentration of Na$_2$O, respectively. Surface tension of pure FeO was reported to be 590–600 mN/m by Kozakevitch. However, unfortunately no literature data are available for the value of $\Gamma_{\text{Na}_2\text{O}}^{\text{sat}}$. Surface tension of the FeO–Na$_2$O system shown in Fig. 7 is expressed by Langmuir-Szyszkowski equation as Eq. (12),

$$\sigma (\text{mN/m}) = 594 - 85.7 \ln(1 + 52.9 X_{\text{Na}_2\text{O}})$$

From this equation, $\Gamma_{\text{Na}_2\text{O}}^{\text{sat}}$ was calculated to be $6.16 \times 10^{-6}$ mol/m$^2$ at 1673 K. Because $\Gamma_{\text{Na}_2\text{O}}^{\text{sat}}$ is unclear as a function of temperature, we assumed that $\Gamma_{\text{Na}_2\text{O}}^{\text{sat}}$ at 1673 K is the same as the value at 1673 K. Thereby, the surface tension of the FeO–Na$_2$O system equilibrated with CO–CO$_2$ gas (CO$_2$/CO=1) is expressed approximately as Eq. (13) at 1673 K,

$$\sigma (\text{mN/m}) = 600 - 90.8 \ln(1 + 29.0 X_{\text{Na}_2\text{O}})$$

Estimated surface tension of the FeO–Na$_2$O system was shown in Fig. 9. The estimated line is reasonable comparing with measured value shown in Fig. 9.

On the other hand, the change of surface potential when the surface is saturated with Na$_2$O could be estimated from Eq. (10) and the calculated value of $\Delta \Phi_{\text{Na}_2\text{O}}^{\text{sat}}$ was $-0.134$ V. Considering dipole moment changes at the surface with the addition of Na$_2$O, the following equation is obtained,

$$\Delta m_{\text{Na}_2\text{O}} = \frac{\varepsilon_0 \Delta \Phi_{\text{Na}_2\text{O}}^{\text{sat}}}{N \Gamma_{\text{Na}_2\text{O}}^{\text{sat}}}$$

where, $\varepsilon_0$ and $N$ are the permittivity of free space (8.854 x $10^{-12}$ F/m) and Avogadro’s number, respectively. Therefore, from Eq. (14), the dipole moment per one Na atom $\Delta m_{\text{Na}_2\text{O}}$ could be calculated. The deduced value was $-3.20 \times 10^{-31}$ C•m or $-0.0959$ Debye. Comparing with $-0.18$ Debye reported by Sun and Belton, the value of $\Delta m_{\text{Na}_2\text{O}}$ is in good agreement with their deduced value within their large experimental error range due to the limited measured data, and the order of magnitude is, as they mentioned, physically reasonable with the obtained data of 0.103 Debye per one O atom on Pt(111) up to the coverage of $1 \times 10^{-2}$ mol/m$^2$ and of 0.62 Debye per atom on Pt(100) below $2 \times 10^{-9}$ mol/m$^2$ from the investigation of work function change by the adsorption of oxygen on the surface of platinum by Derry and Ross.

5. Conclusions

The effect of Na$_2$O addition on the reaction rate of CO$_2$ dissociation on the surface of the FeO–Na$_2$O and the FeO–SiO$_2$–Na$_2$O (mol%FeO : mol%SiO$_2$=65 : 35) was investigated by using isotope exchange technique at 1773 K with $P_{\text{CO}}/P_{\text{CO}_2}=1$ atmosphere.

The rate constant drastically increased with increasing Na$_2$O content of the FeO–Na$_2$O melt. On the other hand, rate constant gently increased for the FeO–SiO$_2$–Na$_2$O melts. For both systems, the Fe$^{3+}$/Fe$^{2+}$ ratio was slightly increased with increasing Na$_2$O content.

The rate constants were estimated from the Fe$^{3+}$/Fe$^{2+}$ ratio of molten oxides for both systems and the strong promoting effect of Na$_2$O was clarified for the FeO–Na$_2$O system, while the rate constants were almost the same as estimated for the FeO–SiO$_2$–Na$_2$O system.

Rate constant of CO$_2$ dissociation for the FeO–Na$_2$O system was analyzed by “smoothed surface potential model” and the measured results were expressed by this model reasonably well. Based on the analyzed results, surface tension of FeO–Na$_2$O system equilibrated with CO–CO$_2$ gas (CO$_2$/CO=1) was estimated at 1773 K.

From the relationship between the rate constant and the surface coverage of Na$_2$O, the change of surface potential when the surface is saturated with Na$_2$O, $\Delta \Phi_{\text{Na}_2\text{O}}^{\text{sat}}$, was estimated as $-0.134$ V and the calculated dipole moment per one Na atom $\Delta m_{\text{Na}_2\text{O}}$ was $-0.0959$ Debye. This value was in good agreement with previously reported data, and also physically reasonable.

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