Effect of P_2O_5 on Reduction Rate of FeO Containing Slags with CO Gas

Tasuku Hamano, Kenji Matsuzaki, Takashi Maki, Yasushi Iwamoto and Kimihisa Ito
Department of Material Science, Waseda University
Okubo 3-4-1, Shinjuku, Tokyo, 169-8555 Japan
Tel: +81-3-5286-3312
Fax: +81-3-3205-6787
e-mail: tasuku@ itolab.cache.waseda.ac.jp
http://www.itolab.cache.waseda.ac.jp

Abstract
The kinetic study of Fe_tO-containing slag is valuable if we consider slag-gas and slag-metal reactions in the iron and steelmaking process. In the present work, the reduction rate of Fe_tO-SiO_2-TiO_2-MO_X (MO_X = CaO, MgO, $AlO_{1.5}$, $PO_{2.5}$) melts in equilibrium with solid iron by CO gas was measured using the thermobalance system at 1673 K. A rate equation was developed based on the results obtained. The mechanisms of the reaction and the effect of P_2O_5 as a surfactant were discussed.

INTRODUCTION

In the iron and steelmaking process the kinetic study of Fe_tO-containing slag plays an important role in slag-gas and slag-metal reactions. Since the reaction of Fe_tO in slag with C dissolved in metal and with CO gas generated at the interface affects the overall rate of slag-metal reactions, the effect of the components (especially P_2O_5) on the reduction rate is important in analysis of the hot-metal dephosphorization process. Among the investigations made of the reaction, for example Nagasaka et al.[1] measured the reduction rate for various liquid slags containing Fe_tO in equilibrium with solid iron with an Ar-CO mixture gas using the thermobalance technique. Sasaki et al.[2], El-Rahaiby et al.[3], Sun et al.[4] and Mori et al.[5] measured the dissociation rate of CO_2 on liquid melts using the isotope exchange technique. There are, however, few studies of TiO_2-containing slag and P_2O_5-containing slag.

In the present work, the reduction rate of Fe_tO-SiO_2-TiO_2-MO_X (MO_X = CaO, MgO, $AlO_{1.5}$, $PO_{2.5}$) melts in equilibrium with solid iron by CO gas was measured using the thermobalance system at 1673 K, and the rate equation was developed based on the results. The mechanisms of the reaction and the effect of P_2O_5 as a surfactant are discussed.

EXPERIMENTS

A thermobalance consisting of an electric balance and a SiC electric resistance furnace was used in the experiment as shown in Fig.1. The temperature was controlled by a proportional-integral-differential (PID) controller which maintained it within ±1K. The temperature was measured by a Pt/Pt-13%Rh thermocouple located just above the crucible. A slag sample of about 2.5g charged in an iron crucible (I.D. 16mm, depth 5mm) was heated and melted under Ar atmosphere. After equilibrium between the liquid slag and the iron crucible had been attained at the selected temperature, an Ar-CO mixture of a desired composition was blown onto the surface of the sample through a stainless steel nozzle (I.D. 2.7mm) from a distance of 10mm above the surface. The P_{CO} and the gas flow rate were controlled by a mass flow controller. The slag samples were prepared by mixing the synthesized Fe_tO, $3FeO$-P_2O_5, reagent grade SiO_2, TiO_2, CaO, MgO and Al_2O_3. The rate of reduction was then measured by reading the decrease in weight of the sample in the crucible connected to the electric balance by Pt wire.

The rate of reduction was calculated by Eq.[1] from the experimental results of the initial stage of the reduction, in which change in the slag composition was negligible as shown in Fig. 2,

$$r = -\left(dn_0 / dt\right)/S \qquad [1]$$

where r is the apparent rate of reduction (mol/m^2·sec), n_O is the number of moles of oxygen in the sample (mol), t is the reduction time (sec), and S is the surface area of the slag sample (m^2).

RESULTS AND DISCUSSION

Figure 3 shows the dependence of the apparent rate of reduction on P_{CO} at 1673K. The rate is proportional to P_{CO} in a low pressure region

$$r = k_a P_{CO} \qquad [2]$$

where k_a is the apparent rate constant (mol/m²·sec·Pa). However, as P_{CO} increases, the rate gradually decreases from the linear relation because of the effect of mass transfer in the liquid phase. Therefore, the rate of reduction at very low P_{CO} (3.85×10^2 to 1.22×10^3 Pa), in which Eq.[2] is valid, was measured to minimize the effect of mass transfer in the liquid phase.

Figure 4 shows the apparent rate constants as a function of X_{Fe_tO} at 1673K for Fe$_t$O-SiO$_2$-TiO$_2$-MO$_X$ melts. They increase with X_{Fe_tO} and the addition of CaO, MgO and AlO$_{1.5}$; P$_2$O$_5$ however, reduces the rate constant.

Figure 5 shows the effect of MO$_X$ concentration in the Fe$_t$O-SiO$_2$-TiO$_2$-MO$_X$ melts on the apparent rate constants at 1673K, where $X_{Fe_tO}=0.7$ and $X_{TiO_2}/X_{SiO_2}=1$. The rate constants increase with mol%CaO, mol%MgO and mol%AlO$_{1.5}$ and the effect of additives on raising them are CaO-MgO-AlO$_{1.5}$, whereas P$_2$O$_5$ decreases the rate constant significantly. The same tendency was reported by Nagasaka et al.[6] and Sun et al.[7].

Nagasaka et al. employed the regression analysis to the data for various Fe$_t$O containing melts and reported that k_a is directly proportional to $[(X_{Fe^{3+}})^2/(X_{Fe^{2+}})^3]^{1/3}$, where $X_{Fe^{3+}}$ and $X_{Fe^{2+}}$ are the concentration of Fe^{3+} and Fe^{2+} in the melt equilibrated with solid iron, however, the physical meaning of the parameter $(X_{Fe^{3+}})^2/(X_{Fe^{2+}})^3$ has not been clearly understood. Since an iron crucible was also used in this experiment. The overall reaction for the reduction is expressed in Eq.[3]

$$(Fe_tO) + CO(g) = tFe + CO_2(g) \qquad [3]$$
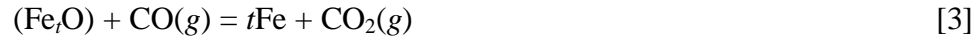
According to Min and Fruehan[8], the slag-gas reaction can be further broken down, and Eq.[4] is the rate determining step.

$$CO(on\ the\ surface) + O^{2-}(on\ the\ surface) = CO_2(g) + 2e^- \qquad [4]$$
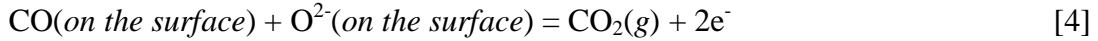
If the overall reaction is governed by Eq.[4], the rate of reduction is described by Eq.[5], in which the effect of surface coverage is assumed to be negligible,

$$R = k_4 P_{CO}\, a_{O^{2-}} - k_4'\, P_{CO_2} \qquad [5]$$

where R is the overall rate of reduction (mol/m²·sec), k_4 and k_4' are the forward and reverse rate constants of reaction [4] (mol/m²·sec·Pa), respectively, and $a_{O^{2-}}$ is the activity of O^{2-} on the surface. In the present work, P_{CO_2} can be defined as 0 since the Ar-CO mixture was used. Thus, R becomes:

$$R = k_4 P_{CO}\, a_{O^{2-}} \qquad [6]$$

Here, if we assume that the $a_{O^{2-}}$ at the surface is proportional to that in a bulk phase, the equilibrium between ferric and ferrous ions in basic slags is expressed by Eq.[7][9].

$$Fe^{2+}+1/4O_2+3/2O^{2-}=FeO_2^- \qquad [7]$$

Since the melts are in equilibrium with solid iron in this study, the reaction [8] is

appropriate to evaluate $a_{O^{2-}}$ in a bulk slag.

$$3Fe^{2+}+4O^{2-}=Fe(s)+2FeO_2^- \tag{8}$$

Equation [8] is valid in the melts of the present work because $X_{Fe^{3+}}/X_{Fe^{2+}}$ increases with the addition of a basic oxide such as CaO or MgO[10]. If O^{2-} on the surface is governed by O^{2-} in the bulk as assumed before, the activity of O^{2-} should be proportional to $(X_{Fe^{3+}})^2 / (X_{Fe^{2+}})^3$ to the one-fourth power, assuming that the activity coefficients of FeO_2^- and Fe^{2+} can be regarded as constant:

$$a_{O^{2-}} \propto \left[(X_{Fe^{3+}})^2 / (X_{Fe^{2+}})^3 \right]^{\frac{1}{4}} \tag{9}$$

If the apparent rate of reduction, r, can be identified as R, the apparent rate constant, k_a becomes:

$$k_a \propto \left[(X_{Fe^{3+}})^2 / (X_{Fe^{2+}})^3 \right]^{\frac{1}{4}} \tag{10}$$

Thus, $\left[(X_{Fe^{3+}})^2 / (X_{Fe^{2+}})^3 \right]^{1/4}$ is considered to be proportional to the driving force of the reduction, $a_{O^{2-}}$. Figure 6 shows the apparent rate constants as a function of $(X_{Fe^{3+}})^2 / (X_{Fe^{2+}})^3$ at 1673K. The values of $X_{Fe^{3+}}$ and $X_{Fe^{2+}}$ for each slag in equilibrium with solid iron were determined by the equilibrium experiments [10][11]. The plots of data agree well with the solid line in Fig.6 given by Eq.[11],

$$\log k_a = \frac{1}{4} \log \left[\left(X_{Fe^{3+}} \right)^2 / \left(X_{Fe^{2+}} \right)^3 \right] - 5.26 \tag{11}$$

The data are also close to Eq.[12] empirically derived by Nagasaka *et al*. The discrepancy between the theoretical value (1/4) and the empirical one (1/3) can be recognized as the effect of surface coverage and the variation in activity coefficients of Fe ions.

$$\log k_a = \frac{1}{3} \log \left[\left(X_{Fe^{3+}} \right)^2 / \left(X_{Fe^{2+}} \right)^3 \right] - 5.28 \tag{12}$$

The rate constants for P_2O_5 containing slags plotted in Fig. 6 are some distance from both lines because of the strong surf-active nature of phosphate ions.

The change in surface coverage θ by the addition of P_2O_5 can be estimated from the experimentally measured rate constants. The value of $1-\theta$ for FeO-Fe_2O_3-P_2O_5 slag drawn in Fig.7 shows the strong surf-active effect of phosphate. Since the slags investigated in this study contain another surf-active component, SiO_2 and perhaps TiO_2, the value of θ was not calculated. Therefore, the extent of surf-active effect of P_2O_5 on Fe_tO-SiO_2-TiO_2 slag was estimated. The calculated values of $(1-\theta)/(1-\theta_0)$ are plotted as a function of P_2O_5 concentration in Fig.7, where θ is the coverage for P_2O_5 containing slag and θ_0 is that for $80Fe_tO$-$10SiO_2$-$10TiO_2$ slag. $(1-\theta)/(1-\theta_0)$ decreases with the increase in P_2O_5, which suggests that the surface coverage significantly increases with P_2O_5 concentration.

This effect of P_2O_5 has practical importance. When FeO containing slag is used for the hot-metal dephosphorization process, the concentration of phosphate in slag increases with time. Since the oxygen potential at the slag-metal interface which governs the dephosphorization is affected by the reduction of FeO, the surf-active effect of P_2O_5 should be quantitatively understood for the precise control of the process. Measurement of these data for steelmaking slags is work remaining for the future.

SUMMARY

1. The rate constants of Fe_tO-SiO_2-TiO_2-MO_X (MO_X = CaO, MgO, $AlO_{1.5}$, $PO_{2.5}$) melts by CO gas increase with mol%CaO, mol%MgO and mol%$AlO_{1.5}$ and the effect of additives on raising them are CaO-MgO-$AlO_{1.5}$, whereas P_2O_5 reduces the rate constant significantly.
2. The following relation between rate constant and slag composition was derived thermodynamically: $k_a \propto \left[(X_{Fe^{3+}})^2 / (X_{Fe^{2+}})^3 \right]^{\frac{1}{4}}$.
3. The extent of the surf-active effect of P_2O_5 on Fe_tO-SiO_2-TiO_2 slag was estimated.

ACKNOWLEDGEMENTS

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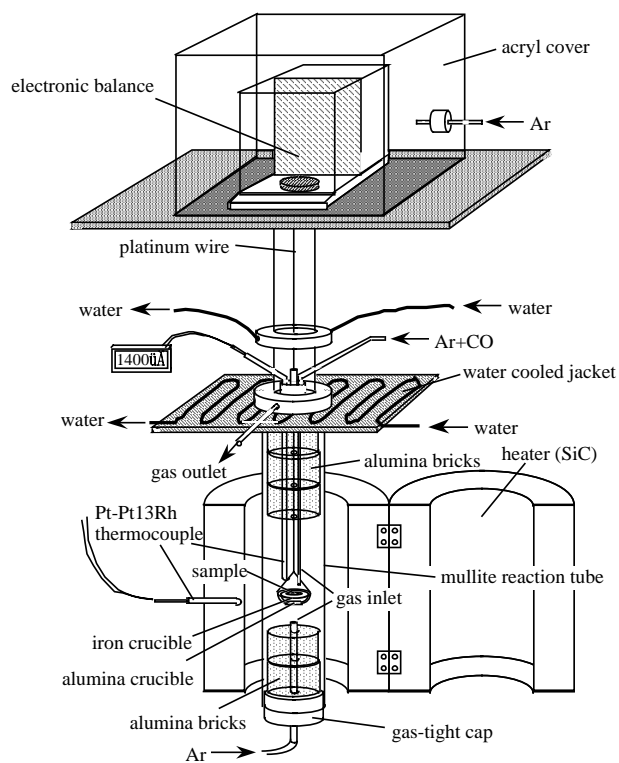
Figure captions

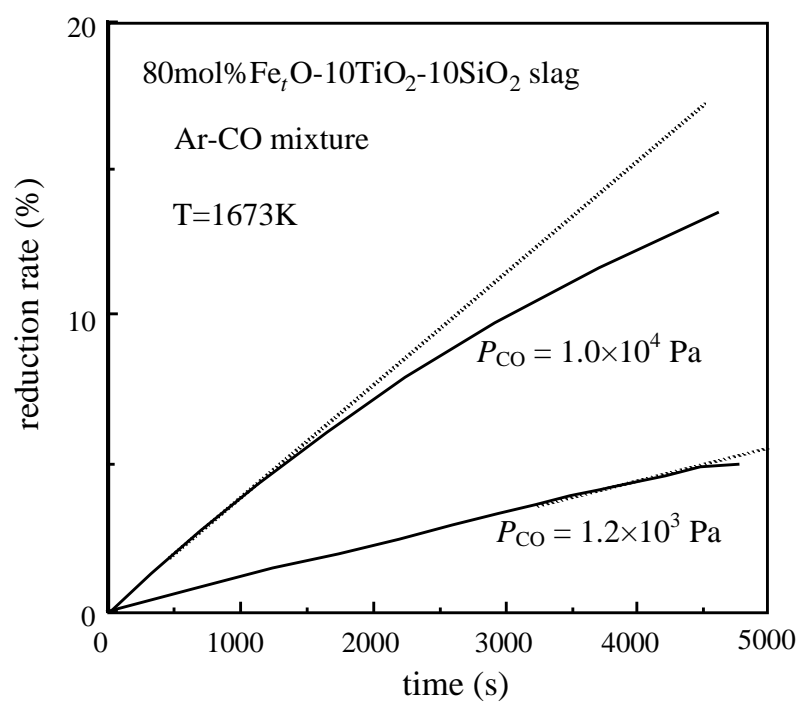Fig.1 Schematic diagram of experimental apparatus.

Fig.2 Reduction curve of Fe_tO-SiO_2-TiO_2 slag reduced with Ar-CO mixture at 1673K.
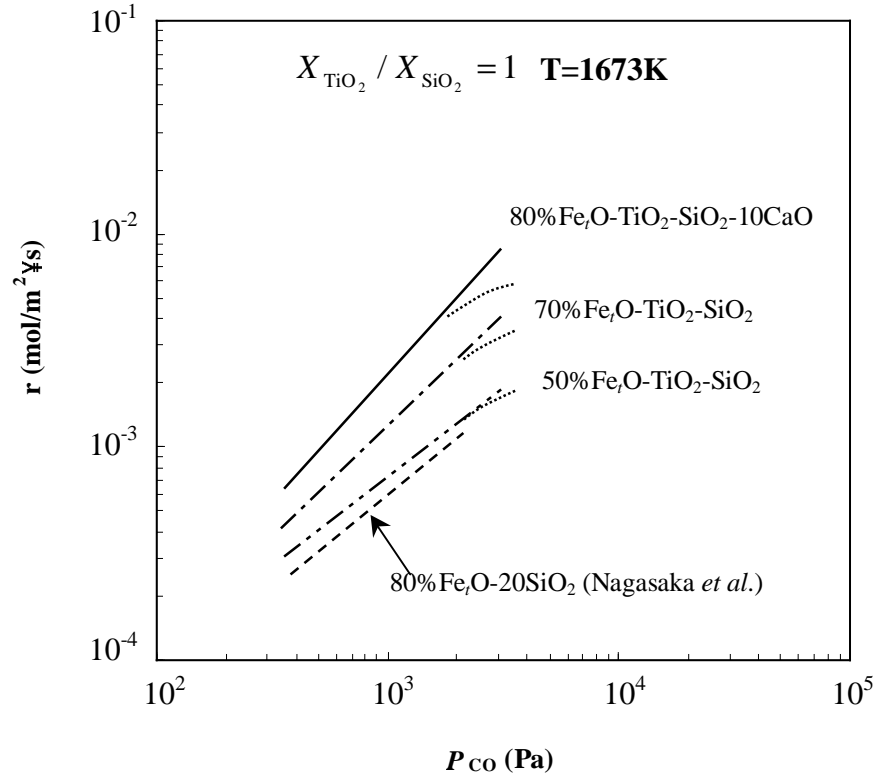
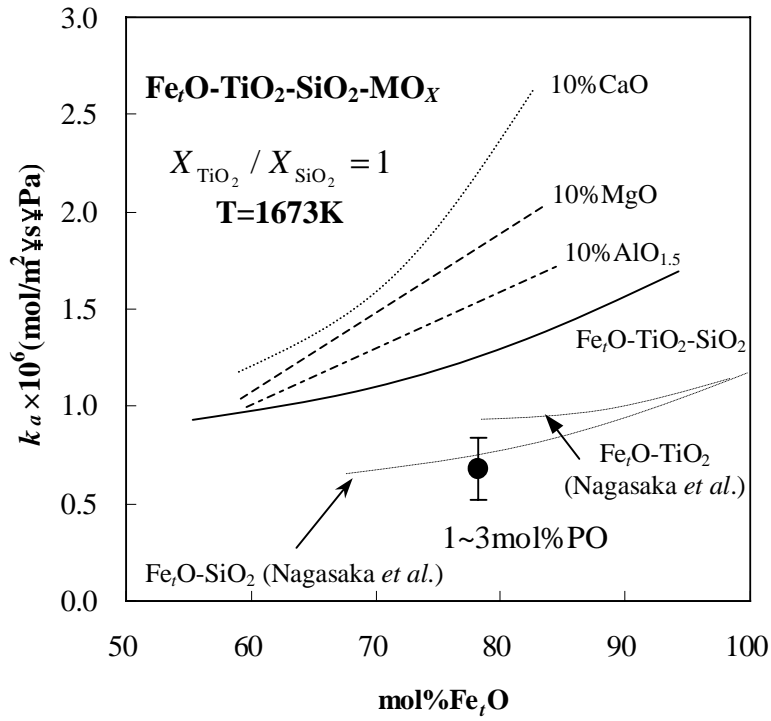Fig.3 Dependence of the apparent rate of reduction on P_{CO} at 1673K.

Fig.4 The apparent rate constants as a function of mol%Fe_tO at 1673K.

Fig.5 Effect of MO_X on the apparent rate constants at 1673K.

Fig.6 The apparent rate constants as a function of $\left(X_{Fe^{3+}}\right)^2 \big/ \left(X_{Fe^{2+}}\right)^3$ at 1673K.

Fig.7 Relation between surface coverage and mol%P_2O_5.

Fig.1 Schematic diagram of experimental apparatus.

80mol%Fe$_t$O-10TiO$_2$-10SiO$_2$ slag

Ar-CO mixture

T=1673K

$P_{CO} = 1.0 \times 10^4$ Pa

$P_{CO} = 1.2 \times 10^3$ Pa

Fig.2 Reduction curve of Fe$_t$O-SiO$_2$-TiO$_2$ slag reduced with Ar-CO mixture at 1673K.

Fig.3 Dependence of the apparent rate of reduction on P_{CO} at 1673K.

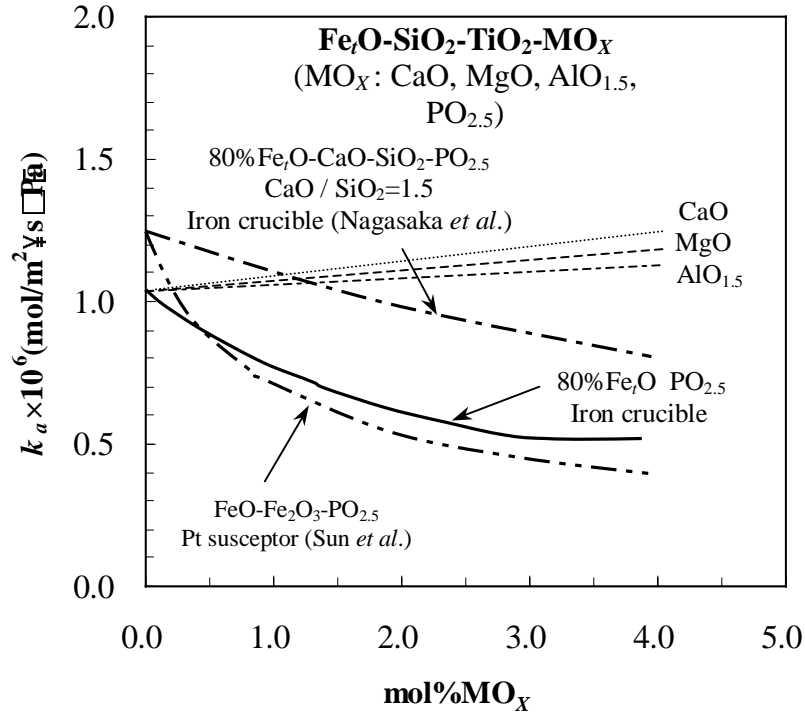Fig.4 The apparent rate constants as a function of mol%Fe_tO at 1673K.

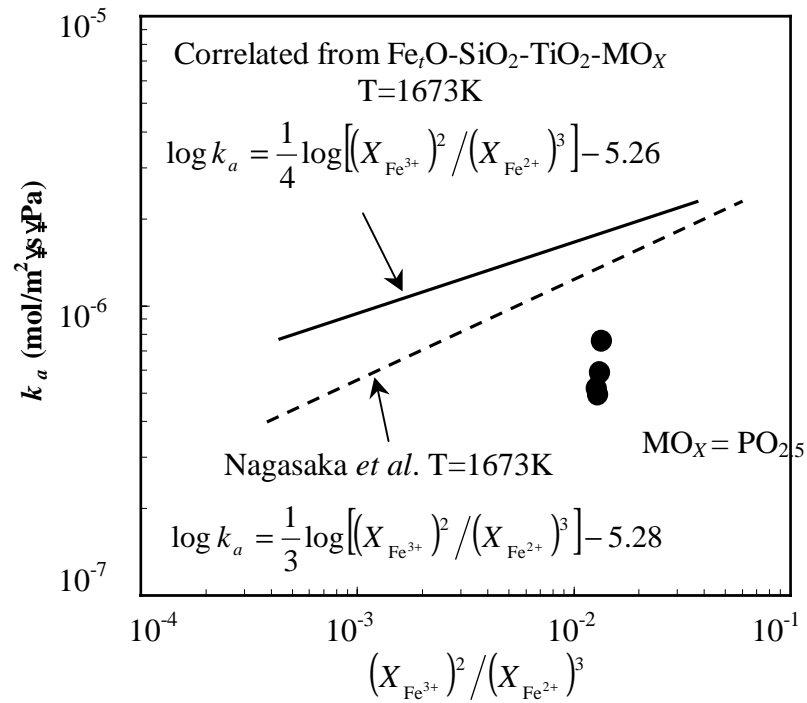Fig.5 Effect of MO_X on the apparent rate constants at 1673K.

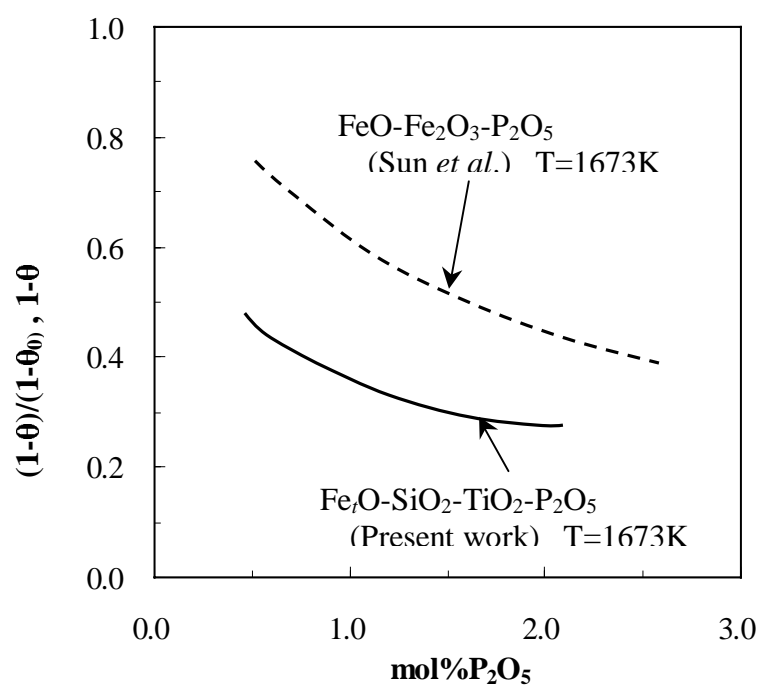Fig.6 The apparent rate constants as a function of $\left(X_{Fe^{3+}}\right)^2 \big/ \left(X_{Fe^{2+}}\right)^3$ at 1673K.

Fig.7 Relation between surface coverage and mol% P_2O_5.