Thermodynamic assessment of V_2O_3–TiO_2 system

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Abstract: The composite oxides involving the V_2O_3, TiO2 and other oxides could be used as the oxidation catalyst. The phase diagram of the V_2O_3–TiO_2 pseudo-binary system is the fundamental to these practical applications; however, no diagram fully assessed of this system is published. Therefore, a set of critically evaluated thermodynamic parameters of the V_2O_3–TiO_2 pseudo-binary system is urgently needed. In order to obtain an assessed V_2O_3–TiO_2 diagram which corresponds with the experimental data well, the existing phase diagram and thermodynamic data of V_2O_3-TiO_2 system are assessed, and the phase diagram are calculated and optimized by using the CALPHAD technology, and some compounds with argument are discussed. In this calculation, the liquid phase, V_2O_3 and TiO_2 are treated with the substitutional solution model. The compound V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$ are treated with the stoichiometric compounds. A self consistent set of the optimized thermodynamic parameters has been derived, which is in better agreement with most of the experiments. Compared with experimental data and the results in this work as well as the results reported previously, it is demonstrated that the present thermodynamic assessment is in better agreement with most of the experiments.

Keywords: Phase diagram, V_2O_3–TiO_2, thermodynamics, substitutional solution model

1. Introduction

Vanadium and titanium exhibit variable-valence, i.e., the ion with three or four valence is common, therefore there exist many oxides of vanadium and titanium. This results to the existence of many pseudo-binary sections in Ti-V-O ternary system. Most of pseudo-binary system which has been studied is the V_2O_3-Ti_2O_3 system. Many researchers have paid the attention to V_2O_3-Ti_2O_3 pseudo-binary systems [1-3]. The V_2O_3-TiO_2 system is an important pseudo-binary system in Ti-V-O ternary system. Chen [4] has studied the binary compounds of V_2O_3-TiO_2 pseudo-binary system. It has been reported that the vanadium based systems are the most selective catalysts for the oxidation of hydrocarbons [5].The V_2O_3-TiO_2 system is often used for catalytic purposes [6, 7]. In spite of a lot of literature on catalytic reactions involving this system, no satisfactory phase diagram was available. The research of V_2O_3-TiO_2 system is necessary for us to establish the thermodynamic database of Ti-V-O system.

Phase reactions were investigated by Bond [8] who reported that the Rutile formation under feed gas conditions associated with a loss of oxygen. The change of the metastable Anatase to Rutile is the subject of the

work of Shannon [9] ,who found that single crystals of Anatase were transformed to Rutile at 900-950℃.

In the preparation of oxidation-reduction catalyst involving V_2O_3-TiO_2 system, Najjar [10] studied the phase diagram of V_2O_3-TiO_2 system. Later, Coetsee [11] constructed a partial V_2O_3–TiO_2 phase diagram from the experimental data. Recently, through DTA and X-ray measurements, the phase diagram of the V_2O_3-TiO_2 system under reducing conditions has been proposed by Habel [12].

But, unfortunately, there isn't a complete experimental phase diagram of V_2O_3–TiO_2 system.The assessment of V_2O_3-TiO_2 pseudo-binary systems was scarcely reported. In this work, the phase diagram of the V_2O_3-TiO_2 system is calculated and optimized by means of the CALPHAD method using the experimental data reported by Najjar [10] and Habel [12].

2. Phase Diagram Information

There is very little experimental data about V_2O_3-TiO_2 system. Up to now, there isn't a complete experimental phase diagram of V_2O_3-TiO_2 system. Early in 1975， Kosuge[13] studied the V_2O_3-TiO_2 System using Electron-Diffraction and Electron-Microscopic.

In the preparation of oxidation-reduction catalyst involving V_2O_3-TiO_2 system, Najjar [10] reported the phase diagram of V_2O_3-TiO_2 system, as shown in Fig. 1.According to Najjar, there are three binary solution phases, V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$, in the V_2O_3-TiO_2 system.

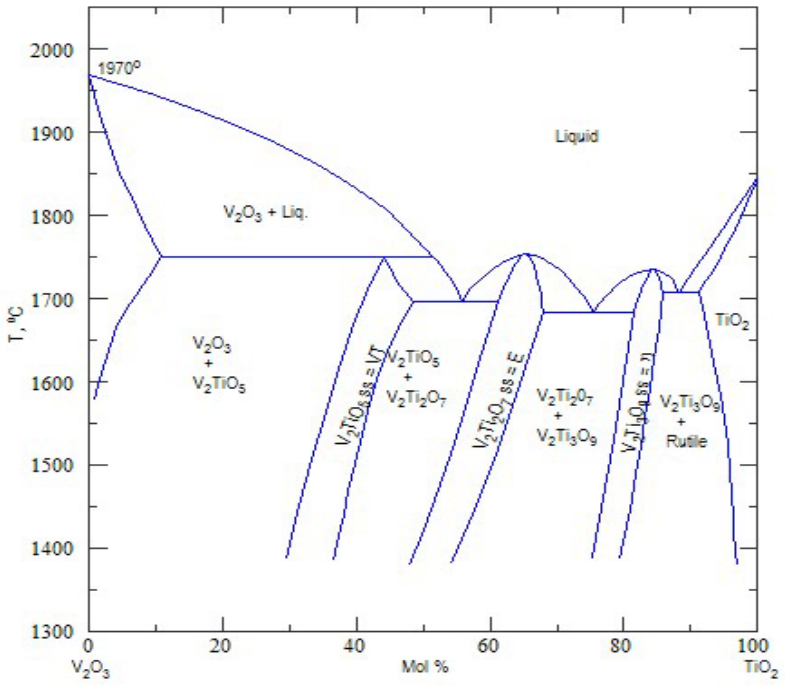

Fig.1 Phase diagram of V_2O_3-TiO_2 system according to Najjar [10].

Later, Coetsee [11] constructed a partial V_2O_3–TiO_2 phase diagram from the experimental data. The phase fields

are identified as M_2O_3, M_2O_3+M_3O_5, and Magneli phases (where M=Ti, V).

Recently, through DTA and X-ray measurements, the phase diagram of the V_2O_3–TiO_2 system under reducing conditions has been proposed by Habel [12], as shown in Fig. 2. In the phase diagram, there are three binary stoichiometric compounds, V_2TiO_5, $V_2Ti_7O_{17}$ and $V_2Ti_3O_9$. At low temperatures(< 600 ℃), no other phase than TiO_2 and V_2O_3 were observed. This indicates a total miscibility gap.

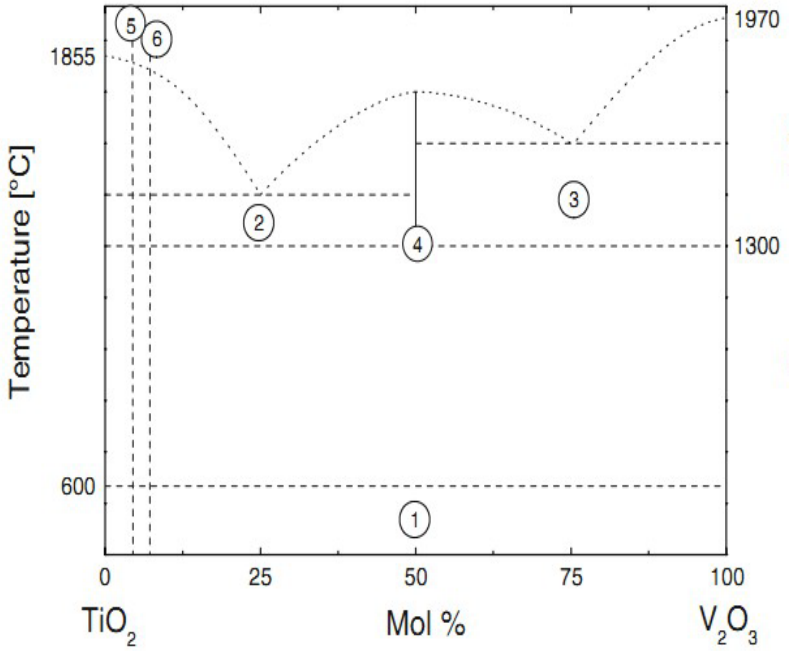

Fig. 2 Phase diagram of the system V_2O_3-TiO_2 according to Habel [12]: (1) V_2O_3+TiO_2; (2) TiO_2 +V_2TiO_5; (3) V_2TiO_5 +V_2O_3; (4) V_2TiO_5; (5) $V_2Ti_7O_{17}$; (6) $V_2Ti_3O_9$

3. Thermodynamic Modeling

3.1 Lattice Stabilities

The stable solid structure of pure V_2O_3 is corundum, and TiO_2 is rutile. For these pure components, it is reasonable to describe their Gibbs energy as a function of temperature, which is shown in eq. (1), the coefficients of stable phase are listed in Table 1, which are cited from Cancarevic[14], the coefficients obtained basing on the result of Brewer [15]also listed in this table:

$$ {}^{0}G_i^{\Phi}(T) = G_i^{\Phi}(T) - H^{SER} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} \qquad (1) $$

Where H^{SER} is the molar enthalpy of the stable element reference (SER) of the pure element in its stable state at 298.15 K and T is the absolute temperature.

Table 1 Summary of Lattice Stabilities of V_2O_3 and TiO_2 Used in the Present Assessment

V_2O_3(corundum):	
$-1.27\times10^{6}+887.15552\mathrm{T}-144.4294\mathrm{T}\ln(\mathrm{T})+9.41\times10^{-3}\mathrm{T}^{2}$ $-1.82\times10^{-6}\mathrm{T}^{3}+1.73\times10^{6}\mathrm{T}^{-1}(298-2230\mathrm{K})$	This work
V_2O_3(liquid):	
$-1.17\times10^{6}+965.34676\mathrm{T}-158.89087\mathrm{T}\ln(\mathrm{T})-2.08\times10^{-4}\mathrm{T}^{2}$ $+7.19\times10^{-9}\mathrm{T}^{3}-1.10\times10^{6}\mathrm{T}^{-1}(298.15-5000\mathrm{K})$	This work
TiO_2(rutile):	
$-976986.6+484.74037\mathrm{T}-77.76175\mathrm{T}\ln(\mathrm{T})-67156800\mathrm{T}^{-2}$ $+1683920\mathrm{T}^{-1}(298.15-3000K)$	Cancarevic[14]
TiO_2(liquid):	
$-915964.2+456.54037\mathrm{T}-77.76175\mathrm{T}\ln(\mathrm{T})-67156800\mathrm{T}^{-2}$ $+1683920\times\mathrm{T}^{-1}(298.15-3000\mathrm{K})$	Cancarevic[14]

3.2 Thermodynamic Modeling of Binary Compounds

In this calculation, three intermediate compounds are involved, including V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$. Because of the lack of experimental data, very limited solid solubility is reported in these compounds, so all compounds were described as stoichiometric compounds, which Gibbs energy is given in the following equation:

$$G=\sum_i x_i G_i^{0,\Phi}+a+bT \qquad (2)$$

where $G^{0,\Phi}i$ represents the Gibbs energy of simple oxides which are the component of the complex oxides, x_i means the mole fraction of the simple component, for example,V_2TiO_5 is formed with V_2O_3 and TiO_2, both mole fraction is 1. a and b are the parameters, which are needed to be optimized by using the formation energy and the decomposition temperature.

3.3 Thermodynamic Modeling of Binary Solution Phases

The liquid phase and other solid solutions in this system are described according to the substitutional solution model, and their Gibbs free energy can be expressed by the following equation:

$$G^{\Phi}=\sum_i x_i G_i^{0,\Phi}+RT\sum_i x_i\ln x_i+G^{ex,\Phi} \qquad (3)$$

Where x_i is the mole fraction of the species i,$G_i^{0,\Phi}$ is the standard Gibbs energy of the pure component i with structure Φ,and R is gas constant, and T is the absolute temperature, $G^{ex,\Phi}$is the excess Gibbs energy of the phase Φ.The excess Gibbs energy is given by the general formula using the Redlich–Kister polynomial [16]:

$$G^{ex,\Phi} = \sum_{i,j=1(i\neq j)}^{n} x_i x_j \sum_{k=0}^{m} L_{(i,j)}^{k} (x_i - x_j)^k \qquad (4)$$

$L_{(i,j)}^{k}$ are binary interaction parameters for the i-j binary, which is to be optimized ,for each phase considered in the systems and k<2.

4. Optimization of Thermodynamic Parameters

There is a huge difference between Fig. 1 and Fig. 2.There are three binary solution phases, V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$, in the V_2O_3-TiO_2 system reported by Najjar [10].While, Habel [12] thought there were three binary stoichiometric compounds, V_2TiO_5, $V_2Ti_7O_{17}$ and $V_2Ti_3O_9$. Both confirmed the existence of two compounds V_2TiO_5 and $V_2Ti_3O_9$ in the V_2O_3-TiO_2 system. In our present work, we consider that $V_2Ti_2O_7$ is stable existence according to Najjar's result, and dispute the existence of $V_2Ti_7O_{17}$. Whether these two compounds are stable existence needs further experimental proof.

The lack of experimental data the incompleteness of experimental phase diagram of this system, bring a big challenge for the assessment of V_2O_3–TiO_2 system. In our assessment, three binary compounds, V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$, have been considered. To simplify the optimization, the three binary compounds were all treated as stoichiometric compounds. The phase diagram of the V_2O_3-TiO_2 system were calculated and optimized by means of the CALPHAD method using the experimental data reported by Najjar [10] and Habel [12].

In the present work, all thermodynamic parameters are optimized by Pan-optimizer included in the Pandat phase equilibrium calculation software, which is a C/C++ software package for evaluating thermodynamic, kinetic and thermo-physical model parameters from experimental measurements. The optimization is conducted until the sum of the squares of the errors between the calculated and the experimental thermodynamic properties and the phase equilibria is minimized.

Table 2. The thermodynamic parameters of V_2O_3-TiO_2 system in this work.

Phase	Thermodynamic parameters
Liquid	${}^{0}G_{V_2O_3}^{Liquid}$
	${}^{0}G_{TiO_2}^{Liquid}$
	${}^{0}L_{V_2O_3,TiO_2}^{Liquid} = -32815 - 10T$
	${}^{1}L_{V_2O_3,TiO_2}^{Liquid} = +73000 - 16T$
	${}^{2}L_{V_2O_3,TiO_2}^{Liquid} = -20000 + 2.5T$

V_2O_3	${}^0G_{V_2O_3}^{Corundum} - 4000$ ${}^0G_{TiO_2}^{Corundum} = {}^0G_{TiO_2}^{Rutile} + 3000$ ${}^0L_{V_2O_3,TiO_2}^{Corundum} = 120000 - 55.6T$
TiO_2	${}^0G_{V_2O_3}^{Rutile} = {}^0G_{V_2O_3}^{Corundum} + 30000$ ${}^0G_{TiO_2}^{Rutile} + 1000$ ${}^0L_{V_2O_3,TiO_2}^{Rutile} = -48072 - 15T$
V_2TiO_5	${}^0G^{V_2TiO_5} = 0.55\,{}^0G_{V_2O_3}^{Corundum} + 0.45G_{TiO_2}^{Rutile} - 19309 + 1.7T$
$V_2Ti_2O_7$	${}^0G^{V_2Ti_2O_7} = 0.333\,{}^0G_{V_2O_3}^{Corundum} + 0.667G_{TiO_2}^{Rutile} - 5167 - 7T$
$V_2Ti_3O_9$	${}^0G^{V_2Ti_3O_9} = 0.15\,{}^0G_{V_2O_3}^{Corundum} + 0.85G_{TiO_2}^{Rutile} - 8701 - 2T$

This procedure can be conducted as follows: Firstly, V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$ were described as stoichiometric compounds and the experimental data [10, 12] are used to optimize thermodynamic parameters of V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$ phase; Secondly, solid solubility in V_2O_3 and TiO_2 terminal solid solution are considered, thermodynamic parameters of V_2O_3, TiO_2 and Liquid phase were optimized. All parameters optimized in this work are listed in Table 2.

5. Results and Discussions

There are three binary solution phases, V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$, in the V_2O_3-TiO_2 system reported by Najjar [10] r. While, Habel [12] thought there were three binary stoichiometric compounds, V_2TiO_5, $V_2Ti_7O_{17}$ and $V_2Ti_3O_9$. Both confirmed the existence of two compounds V_2TiO_5 and $V_2Ti_3O_9$ in the V_2O_3-TiO_2 system. In our present work, we consider that $V_2Ti_2O_7$ is stable existence according to Najjar [10]'s result, and dispute the existence of $V_2Ti_7O_{17}$. In this calculation, the liquid phase, V_2O_3 and TiO_2 are treated with the substitutional solution model. The compound V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$ are treated with the stoichiometric compounds. The calculated phase diagrams of the V_2O_3-TiO_2 systems are illustrated in Figs.3. Here, experimental data from Najjar [10] is included. The calculated equilibria is in good agreement with the majority of experimental results Najjar.

Table 3 lists the temperatures of the invariant reactions calculated in the present work. Table 4 lists the melting point of binary stoichiometric compounds, V_2TiO_5, $V_2Ti_7O_{17}$ and $V_2Ti_3O_9$, calculated in the present work as well as the values reported by Najjar [10] and Habel[12]. It can be seen that the calculated results are in good agreement with the most of the experimental results.

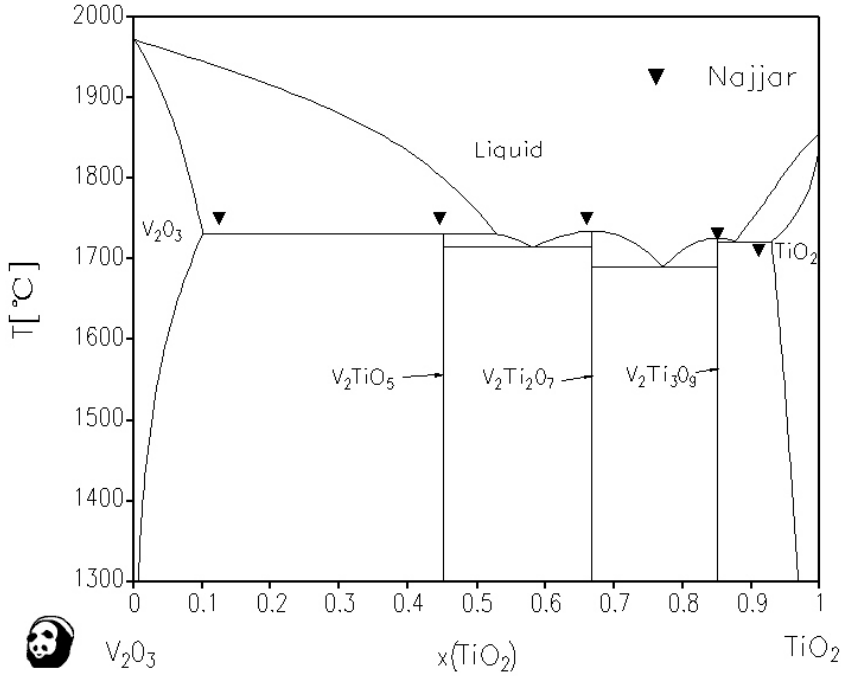

Fig.3 Calculated V_2O_3-TiO_2 phase diagram

Table 3 Calculated results for the invariant reactions in V_2O_3-TiO_2 system.

Reactions	T(℃)	Source
Liquid + V_2O_3 = V_2TiO_5	1730 1750	This work Najjar [10]
Liquid = V_2TiO_5 + $V_2Ti_2O_7$	1714 1700	This work Najjar [10]
Liquid = $V_2Ti_2O_7$ + $V_2Ti_3O_9$	1700 1680	This work Najjar [10]
Liquid = TiO_2 + $V_2Ti_3O_9$	1721 1710	This work Najjar [10]

Table 4 Calculated and experimental results of the melting point for binary stoichiometric compounds in V_2O_3-TiO_2 system.

Compounds	Melting Point(℃)	Source
V_2TiO_5	1731 1750 1750	This work Habel[12] Najjar [10]
$V_2Ti_2O_7$	1734 1750	This work Najjar [10]
$V_2Ti_3O_9$	1726 1730	This work Najjar [10]

6. Conclusions

In order to obtain an assessed V_2O_3-TiO_2 diagram which corresponds with the experimental data well, the existing phase diagram and thermodynamic data of V_2O_3-TiO_2 system are assessed, and the phase diagram are calculated and optimized by using the CALPHAD technology. In this calculation, the liquid phase, V_2O_3 and

TiO_2 phases are treated with the substitutional solution model, V_2TiO_5, $V_2Ti_2O_7$ and $V_2Ti_3O_9$ phases are described as stoichiometric compounds. A self consistent set of the optimized thermodynamic parameters has been derived, which is in better agreement with most of the experiments. Some invariant reactions are calculated. This assessment may provide the theoretical support to the preparation of catalyst. The assessment of V_2O_3-TiO_2 pseudo-binary system is helpful for us to establish the Ti-V-O ternary system database.

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