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KINETIC STUDY OF SYNTHESIS OF TITANIUM CARBIDE BY METHANOTHERMAL REDUCTION OF TITANIUM DIOXIDE

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Abstract: *Reduction of the Titanium dioxide,* TiO_2*, by methane was investigated in this work. The thermodynamic of reaction was examined and found favorable. The reaction of titanium dioxide with methane was carried out in the temperature range 1150°C to 1450°C at atmospheric pressure with industrial high porosity pellets prepared from titanium dioxide powder. The evolved gas analyzing method was used for determination of the extent of reduction rate. The gas products of the reaction are mostly CO and trace amount of* CO_2 *and* H_2O*. The synthesized product powder was characterized by X-ray diffraction (XRD) for elucidating solid phase compositions. The effect of varying temperature was studied during the reduction. The conversion-time data have been interpreted by using the grain model. For first order reaction with respect to methane concentration, the activation energy of titanium dioxide reduction by methane is found to be 51.4 kcal/gmole. No detailed investigation of kinetic and mechanism of the reaction was reported in literatures.*

Keywords: *Titanium Dioxide, Reduction, Methane, Titanium Carbide, Kinetic Study.*

1. INTRODUCTION

Titanium metal has become known as a space-age metal because of its high strength-to-density ratio and inertness to many corrosive environments. Titanium is mainly utilized in the form of titanium dioxide (TiO_2) as paint filler, paper, rubber and plastic industries [1], and the demand for titanium pigment is growing steadily [2]. Titanium minerals are also processed to produce metallic titanium and titanium compounds, particularly titanium carbide (*TiC*) and nitride (*TiN*), which are used in the manufacture of composite materials and ceramics or as catalyst.

Production of Titania white pigments and metal titanium include processing of titanium minerals to titanium tetrachloride. Chlorination of titanium dioxide is carried out almost exclusively by fluidised-bed process, which requires high temperature of 800-1100 °C, and involves the use of petroleum coke (250-400 kg/t TiO_2) as the reducing agent. Existing technology for titanium tetrachloride production requires minerals of high quality, with low impurities level, which are processed prior to chlorination to synthetic rutile or TiO_2-rich slag [3].

Titanium oxycarbide can be chlorinated at low temperatures. Mostert et al.[4-5] reported that carbonitride produced by reduction/nitridation of titanium oxide from ilmenite and titanium slag was chlorinated at 200-500 °C. In the low temperature chlorination, impurity-oxides do not chlorinate or chlorinate very slowly [6]. This permits selective chlorination of titanium oxycarbide, decreases the chlorine consumption and waste generation, and makes the whole technology of ilmenite processing more efficient and environmentally friendly.

Kinetic study of the Titanium dioxide reduction by methane was not reported in literature. The purpose of this work is to obtain kinetic parameters of reduction of Titanium dioxide, TiO_2, with methane, toward assessing the feasibility of using methane to produce metallic titanium and titanium compounds.

2.THERMODYNAMIC CONSIDERATIONS

The reduction of titanium dioxide with carbon carries out in the temperature range 1200 K to 1500 K. The Free enthalpy change and the overall reaction are as follows [7]:

$$TiO_2 + 3C = TiC + 2CO \qquad \Delta H^0_{rxn} = 124\ kcal/gmol \tag{1}$$

Methane also has a strong reducing capability, and can react at lower temperature simply:

$$TiO_2 + 3CH_4 = TiC + 2CO + 6H_2 \qquad \Delta H^0_{rxn} = 190.7\,kcal/gmol \tag{2}$$

Consider a general equation, as follows:

$$\sum \upsilon_R R = \sum \upsilon_P P \tag{3}$$

where R and P represent reactants and products, and υ_R and υ_P are the stoichimetric coefficients of reactants and products, respectively. The equilibrium constant of this reaction can be calculated from the following equation [7]:

$$\log K = \sum \upsilon_P \log K_{f,P} - \sum \upsilon_R \log K_{f,R} \tag{4}$$

where K is the equilibrium constant of the reaction and $K_{f,R}$ and $K_{f,P}$ are equilibrium constants for the formation of reactants and products, respectively. From equation (4), the equilibrium constants of Reactions (1) (carbothermal reduction) and (2) (methanothermal reduction) are computed and tabulated in Table 1 in which K_c and K_{CH_4} are the equilibrium constants for the Reactions (1) and (2) respectively. Table 1 shows that methane reagent has greater reducing capability than carbon, which creates a potential to decrease the operating temperature of reduction of Titanium dioxide.

Table 1 also shows the equilibrium constant for hydrogen reduction (K_{H_2}) of titanium dioxide. From this we can discover that hydrogen reaction with TiO_2 is thermodynamically impossible. Hydrogen reduction of titanium dioxide can be represented as follows:

$$TiO_2 + 2H_2 = Ti + 2H_2O \tag{5}$$

Table 1. Equilibrium constants for carbothermal (1) and methanothermal reduction of (2).

T (K)	K_{CH_4}	$K_C \times 10^4$	$K_{H_2} \times 10^{15}$
1300	716	3	4
1400	14064	100	80
1500	136458831	2000	1000

3. EXPERIMENTAL SETUP

The evolved gas analyzing method was used for determination of the extent of reduction rate. The experimental setup is shown in Figure 1. The vertical type electric high temperature furnace (Model HT 08/17, Ceramic Engineering, Australia) has been used for heating the reactor to the reduction temperatures. The pellets were made using titanium dioxide powder. The system was heated to the desired temperature under an inert gas stream such as argon. Then the isothermal period begins and after temperature stabilization, the reducing gas (a mixture of CH_4/H_2/Ar) is introduced from the top of the reaction tube. The gas streams passed through the Hydropurge gas purifiers filled with 4A molecular sieve to remove moisture. The composition of reducing gas was achieved by precisely controlling the flow rate of each gas with Brooks mass flow controllers. Direct measurement of temperature in the vicinity of the solid pellet was difficult to implement. A thermocouple was shielded by a sheath and the temperature of gas mixture at the inlet of reaction chamber was measured. The reducing gas was the mixture of methane with high purity (99.95%), hydrogen with super high purity (99.999) and argon with high purity. The use of argon as an inert gas facilitated adjusting of gas composition and provided a reference for calculation of off-gas flow rate. The gases were provided by BOC Gases, Australia, in gas cylinders.

The scheme of the reactor used in the experiments is depicted in Figure 2. A recrystallised alumina tube of 8.6 mm inner diameter was used as a sample holder. A porous magnesia plug was fixed at the tube bottom by an alumina pin. The temperature at the inlet of the tube was measured by a type B thermocouple and is referred as the reduction temperature. The inner tube was inserted into an outside recrystallised alumina sheath of 19.0 mm inner

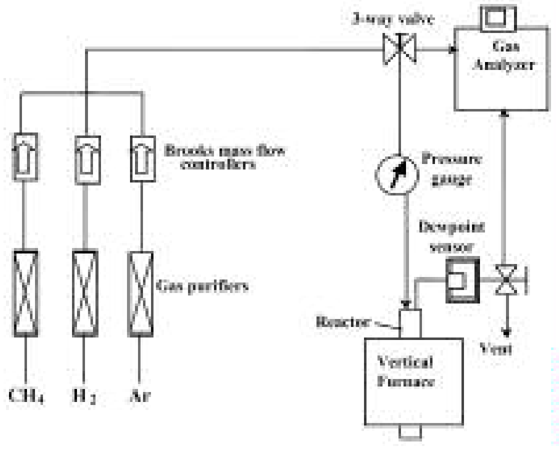

Fig. 1. Flow diagram of experimental system for kinetic study of reduction of titanium dioxide.

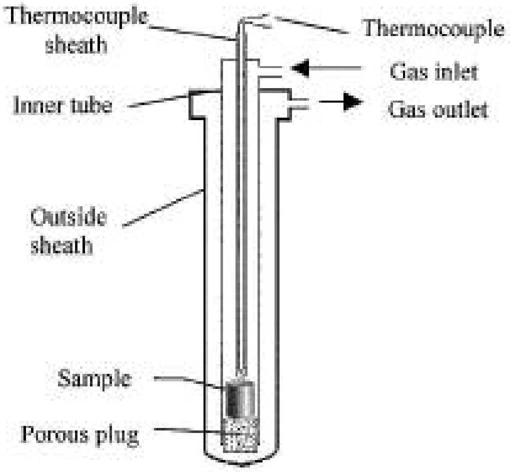

Fig. 2. Schematic of experimental reactor.

diameter. The inner tube, outside sheath and thermocouple sheath were fixed by special metal fittings and sealed with O-rings.

The outlet gas stream also leaves the system from the top of reaction tube, firstly passed through a dew point sensor for evaluating water content of the outlet stream then passed from the online infrared $CO/CO_2/CH_4$ gas analyzer.

The mole fraction of methane in the input gas mixture was fixed at 5 %. The titanium dioxide (TiO_2) powder employed in the study is rutile with a TiO_2 content of 99.9+ % and with a mean particle of about 2 microns that was supplied by Aldrich Chemical Company, Inc. (Milwaukee WI, USA, Catalog number 22422-7). The sizes of particles were calculated by using the average specific surface area of pellet that measured by BET analysis.

Titanium dioxide pellets were made by mechanical pressing of the powder in a pressing mould (1500 kg/cm^2). The pellets were assumed semi-spherical in kinetic modeling.

The reduction experiments were carried out in the temperature range of 1150-1450°C under atmospheric pressure. Experiments were conducted with excessive reducing gas. Preliminary experiments showed that the reaction rate was not affected by the gas flow rate if the flow rate is greater than 1 L/min, therefore a total gas flow rate was maintained at 1 L/min which means that external mass transfer resistance was negligible during the reaction.

Phase composition of products was measured by powder X-ray diffraction (XRD, Simens D5000). A sample was ground to fine powder and closely packed in the cave of a plastic sample holder. The diameter of the cave was 10mm. The X-ray Diffractometer has a monochromator and a copper Kα X-ray source. The voltage and current exerted on to the X-ray emission tube were set at 30 kV and 30 mA, respectively. The scanning was performed from 20 to 80°. The scanning rate of samples of reduced titanium dioxide was set at 0.75° /min with a step of 0.05 °.

4. FORMULATION OF KINETIC MODEL

The methanothermal reduction of titanium dioxide is expressed by Equation (2). The "conversion" is defined as the oxygen loss of a sample at a given time divided by the sample total oxygen when it is unreacted, i.e., total conversion is defined when all oxygen atoms are liberated from reactant sample. Thus, the conversion-time curves can be obtained from the gas analyzer data using the following relation:

$$X = \left[\int_0^t (\dot{n}_{CO} + 2\,\dot{n}_{CO_2} + \dot{n}_{H_2O})dt \right] \Big/ \left(2W_0 / M_{TiO_2} \right) \qquad (6)$$

where $\dot{n}_{CO}$, $\dot{n}_{CO_2}$ and $\dot{n}_{H_2O}$ are molar rate of CO , CO_2 and H_2O production respectively and W_0 is the initial pellet weight, M_{TiO_2} is the molecular weight of titanium dioxide.

The grain model introduced by Szekely et al.

was used to analyze experimental data. This model is well described in the literature [8] and only a brief development is offered here.

The titanium dioxide-methane reaction may be represented by the following equation:

$$A_{(gas)} + bB_{(soid)} \rightarrow cC_{(gas)} + dD_{(solid)} \tag{7}$$

where b and d are stoichiometric coefficients of the solid reactant B and solid product D, respectively and c is the stoichiometric coefficient of the product gas. The modeling is based upon the following assumptions:

1. The pellet retains its initial size throughout the reaction
2. The reaction system is isothermal
3. The external mass transfer resistance is negligible
4. The reaction is irreversible and first order with respect to methane concentration
5. The pseudo-steady approximation is valid.

The solid reactant is visualized as being composed of a large number of highly dense, spherical grains. Each of these grains reacts individually according to unreacted shrinking core model. In the overall pellet, however, the reaction occurs in a zone rather than at a sharply defined boundary. Reactant gas undergoes mass transfer from the bulk gas stream to the pellet surface. From the surface the gas must diffuse to arrive at a sharp interface between the grain particle and the product layer for reaction to take place.

4. 1. Calculation of Rate Constant

In the starting of reaction, for calculating of rate constant we use simple grain model and we neglect the ash layer resistance in the vicinity of zero time for first step. The dimensionless governing equations of the simple grain model for spherical pellet with spherical grains are as follows [9]:

$$\frac{\partial^2 a}{\partial \eta^2} + \frac{2}{\eta}\frac{\partial a}{\partial \eta} = \sigma^2.a.r*^2 \tag{8}$$

$$\frac{\partial r*}{\partial \theta_g} = -a \tag{9}$$

With the initial and boundary conditions:

$$\theta_g = 0,\ r^* = 1 \tag{10}$$

$$y = 0,\ \frac{\partial a}{\partial \eta} = 0 \tag{11}$$

$$y = 1,\ a = 1 \tag{12}$$

where $a = C_A/C_{Ab}$ is dimensionless gas concentration, C_A and C_{Ab} are the concentrations of reactant A in position η with in a pellet and in bulk gas, η is the dimensionless radius of the pellet, $r^* = r_{g_c}/r_{g_0}$ is dimensionless unreacted radius in the grain, r_{g0} and r_{gc} are initial and unreacted core radius of grains, respectively, θ_g is dimensionless time for grain model defined as follows:

$$\theta_g = \frac{bkC_{Ab}t}{\rho_B r_{g_0}} \tag{13}$$

where k is reaction rate constant; b is the time and ρ_B is the true molar density of solid reactant B; σ is the gas-solid reaction modulus. By ignoring structural changes of the pellet, for flat pellet consisting of spherical grains this modulus is defined as:

$$\sigma = R\sqrt{\frac{3.(1-\varepsilon_0)k}{D_{eA} r_{g_0}}} \tag{14}$$

where ε_0 is the pellet porosity which was estimated from the volume and weight of a pellet, and D_{eA} is effective diffusion coefficient of gaseous reactant A in the pellet. D_{eA} was estimated using the random pore model [10]:

$$D_{eA} = D_A \varepsilon_0^2 \tag{15}$$

where D_A was determined by combining molecular and Knudsen diffusion coefficients as follows:

$$\frac{1}{D_A} = \frac{1}{D_{AM}} + \frac{1}{D_{AK}} \tag{16}$$

D_{AM} and D_{AK} are molecular and Knudsen diffusivity of gaseous reactant A in the pellet, respectively. D_{AM} was evaluated using the Chapman-Enskog formula [11] and the D_{AK} was calculated from the following equation [8]:

$$D_{AK} = \frac{4}{3}\left(\frac{8R_gT}{\pi M_A}\right)^{1/2} k_0 \tag{17}$$

where R_g is the gas constant, T is the absolute temperature, M_A is the molecular weight of gaseous reactant and K_0 was calculated from the 'dusty gas model' of Mason et al. [12] as follows:

$$\frac{1}{k_0} = \left(\frac{128}{9}\right) n_d r_g^2 \left(1 + \frac{\pi}{8}\right) \tag{18}$$

n_d , the number of solid grains per unit volume of porous solid, was calculated as follows:

$$n_d = \frac{3(1-\varepsilon_0)}{4\pi r_g^3} \tag{19}$$

By using above equation, the governing equations can be solved and r^* was found in the time near zero as follows:

$$r^* = 1 - \frac{Sinh(\sigma.y)}{Sinh(\sigma)}.\theta_g \tag{20}$$

Extent of reaction or conversion for non-porous grains is defined as local conversion and is the ratio of mass of solid product produced at each time to mass of solid product if the grain converts to solid product completely; so for grains we have:

$$x = 1 - (r^*)^{F_g} \tag{21}$$

where x is the local conversion of the grains and F_g is the grain shape factor, which equals as 1, 2 and 3 for slablike, cylindrical and spherical grains, respectively. However, conversion of pellet (X) is defined as overall conversion and is calculated from local conversion integration over the pellet as follows:

$$X = 1 - 3\int_0^1 \eta^2.(r^*)^3.dy \tag{22}$$

If the Eq. (20) was combined with Eq. (22) and then integrated, the conversion of pellet could be found at the time near zero. Then the slope of conversion time curve in the vicinity of the zero can be shown to be as follows:

$$\left.\frac{dX}{dt}\right|_{t=0} = \frac{9b.k.C_{Ab}}{\rho_B.r_{g_0}}.\frac{[1+\sigma+e^{2\sigma}(\sigma-1)]}{[(e^{2\sigma}-1)\sigma^2]} \tag{23}$$

All of the above nonlinear equation parameters are known except k, which is unknown. By solving the above equation, rate constant for the reduction of titanium dioxide by methane was calculated and listed in Table 2.

5. RESULTS AND DISCUSSION

Reduction of Titanium Dioxide by methane was examined at different temperatures using a methane-hydrogen-argon gas mixture containing only 5 vol% methane. Figure 3 presents the

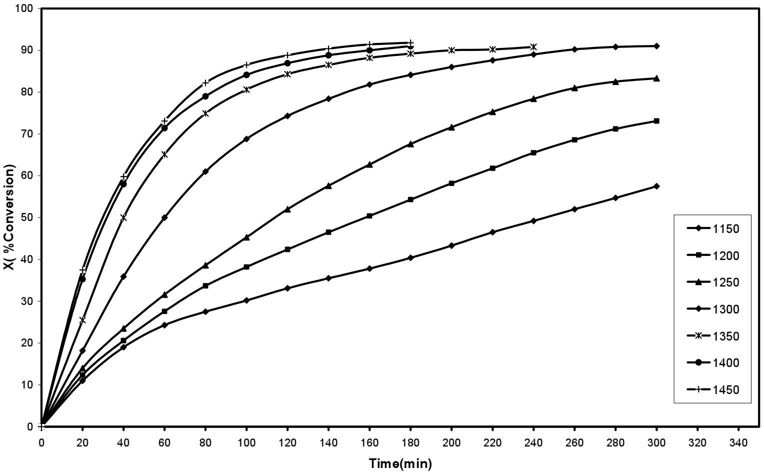

Fig. 3. Isothermal reduction curves of titanium dioxide (5 vol% CH_4,75 vol% H_2 and 20 vol% Ar) at different temperatures.

Table 2. Rate constants for the reduction of Titanium Dioxide by methane at different temperatures

T (°C)	1150	1200	1250	1300	1350	1400	1450
$k(cm/s)\times 10^3$	0.8	2.0	3.7	6.3	13.8	15.2	18.3

conversion-time curve of Titanium Dioxide reduction at different temperature.

The XRD patterns of solid product for different temperatures are presented in figure 4. Their analysis clearly indicates that the majority the solid phase is TiC.

In the metal oxide reduction reactions with methane, the reduction process starts with adsorption of methane on the active sites of the oxide surface and its decomposition described by the following reactions [13]:

$$CH_4(gas) = CH_4(ad) \tag{24}$$

$$CH_4(ad) = CH_3(ad) + H(ad) \tag{25}$$

$$CH_3(ad) = CH_2(ad) + H(ad) \tag{26}$$

$$CH_2(ad) = CH(ad) + H(ad) \tag{27}$$

$$CH(ad) = C(ad) + H(ad) \tag{28}$$

$$2H(ad) = H_2(gas) \tag{29}$$

The overall reaction of methane adsorption and cracking may be presented as:

$$CH_4 \rightarrow \cdots \rightarrow C_{ad} + 2H_2 \tag{30}$$

In which C_{ad} represents active carbon species adsorbed on solid surface, and is substantially different from deposited solid carbon. The reaction rate constant calculated using equation (23) is presented in Table 2.

The effect of temperature on the reaction rate can be evaluated by Arrhenius equation:

$$k = k'e^{-\frac{E_a}{R_g T}} \tag{31}$$

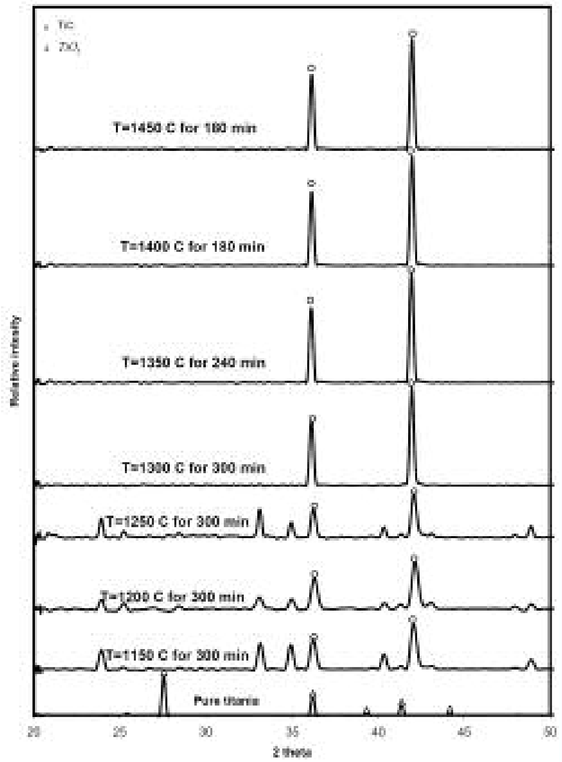

Fig. 4. XRD patterns of TiC formed at different temperatures.

where *k'* is the frequency factor and E_a is the apparent activation energy. Arrehenius plot for this reaction is shown in Figure 5. From the resulting straight line, the temperature dependency of the reaction rate constant is as follows:

$$k = 8.1\times 10^4 e^{-\frac{25876}{T}} \tag{32}$$

From equation (32) the activation energy of the Titanium Dioxide reduction is found to be 51.4 kcal/gmole.

One of the most important parameters of the reduction reaction is the apparent activation energy as it defines the reactor dimensions and the energy consumption. Making comparison for activation energy of methanothermal reduction reaction is more interesting. The activation

Table 3. Comparison of activation energy of methane reduction reactions.

Metal oxide	T (K)	E_a (kcal/gmole)	Reference
Fe_2O_3	1148-1223	52.70	[14]
ZnO	1113-1203	67.09	[15]
PbO	973-1123	51.62	[16]
CoO	1073-1223	37.18	[17]
Cr_2O_3	1143-1248	47.09	[18]
NiO	873-998	63.89	[19]
$BaSO_4$	1173-1248	96.00	[20]

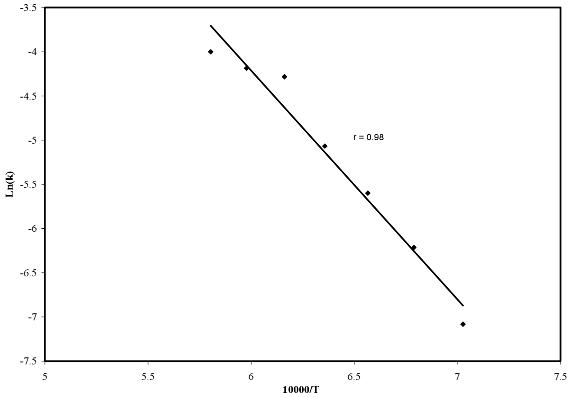

Fig. 5. Arrhenius plot of the rate constant of the reaction of Titanium Dioxide with methane

energy of studied methanothermal reactions are summarized in Table 3. As seen from Table 3, the activation energy values reported for reduction reactions by methane are within the same order of magnitude. Additionally the value reported in this article for reduction of Titanium Dioxide with methane is within the same order of magnitude for reduction of other metal oxide with methane.

6. CONCLUSION

In the present work, titanium dioxide was successfully reduced and carburized into solid *TiC* by methane. The outlet gas analyzing method was used for determining the extent of the reaction. The reduction temperature range is of 1150 to 1450°C and the reaction was carried out under atmospheric pressure. The kinetic parameters of this reaction were calculated by applying the grain model to the experimental results. The activation energy of reduction of Titanium Dioxide by methane was found to be 51.4 kcal/gmole, which is within the same order of magnitude of other metal oxide methanothermal reduction.

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