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KINETIC MODELING OF HYDROGEN TRANSPORT-LIMITED REDUCTION RATE USING *SHRINKING CORE MODEL*

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ABSTRACT

Reduction of titanium dioxide (TiO_2) is important in the production of titanium sub-oxides such as Ti_3O_5 and Ti_2O_3 which have numerous applications. In this research, mathematical modeling of hydrogen (H_2) reduction of TiO_2 has been developed in MATLAB by using a shrinking core model (SCM). The SCM can be used to determine the transport-limited reaction rate for TiO_2 reaction in 100 volume (vol.) % of H_2 atmosphere. H_2 gas was used due to its environmental benefits and faster reaction kinetics. The reduction process was predicted from independently measured physical and thermodynamic properties of TiO_2 and H_2 components. From the theoretical modeling results, the percent of reduction (R') for isothermal conditions was 100% at 20 minutes with a temperature range between 1373-1773 K. Experimental data showed a lowered R' then the model, with maximum R' of 70% at 1773 K after 40 minutes. At 1373 K, experimental R' was about 10%. Nonisothermal reduction model showed a theoretical R' value of 100% after 40 minutes at 1373 K. At 1773 K, the theoretical R' of 100% was obtained after 20 minutes. Non-isothermal reduction modeling showed a better approximation to experimental data than isothermal reduction.

Keywords: Titanium Dioxide; Mathematical Modeling; Matlab

INTRODUCTION

Reduction of titanium dioxide (TiO_2) is important as reduced TiO_2 have attracted many numerous applications. Among the sub-oxides of Ti_3O_5 and Ti_2O_3 has been found to be an ideal candidate for holographic memory applications [1]. In recent times, there was a lot of CO_2 generated from the reduction of TiO_2 by using carbon as the reducing agent [2]. The increase of CO_2 related to carbothermal reduction of TiO_2 will increase greenhouse gases and it is not environmentally friendly. From this industrial point of view, direct reduction of TiO_2 with H_2 will have a few technical

advantages, such as, replacement of carbon as the reducing agent [3]. Besides that, the production of H_2O in the reduction process can be recycled back for H_2 production and does not contribute to greenhouse gases. Iron ore reduction by H_2 is a commercial process *via* the COREX process and the mathematical model developed in this study will be suitable to be applied for gaseous reduction of TiO_2 [4]. The reduction of TiO_2 by H_2 was found to proceed in the following steps shown in Eq. 1 [5]:

$$TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \quad (1)$$

However, the reduction of TiO_2 to Ti_2O_3 was quick and overlapped at high temperatures. Therefore, these steps can be presented as a single step as in Eq. 2 [6].

$$2TiO_{2(s)} + H_{2\,(g)} = Ti_2O_{3(s)} + H_2O_{\,(g)} \;\; , A_{\,(s)} + B_{(g)} = C_{(s)} + B_{(g)} \quad (2)$$

where $A = TiO_{2(s)}$, $B = H_{2(g)}$, $C = Ti_2O_{3(s)}$ and $D = H_2O_{(g)}$.

In the above reaction, TiO_2 was reduced by H_2 into Ti_2O_3. A mass balance of H_2O gas performed on the layers of accumulated Ti_2O_3 during the time increment of Dt (time of reaction). The TiO_2

particle was divided into concentric shells that shrinks during the reduction. Similar kinetic modeling work on TiO_2 and Fe_2O_3 reduction was done by G. Zhang et al. [7] and Gower [8]. The assumption during the kinetic modeling is that the reaction interface and particle temperature remains constant and no H_2O gas accumulates in the product layer [9].

EXPERIMENTAL

The TiO_2 reduction data was obtained from experimental studies done by Sheikh A. Rezan et al. [5,14],Yong Jing Hui [10], Tan Wei Yin [11], G. Zhang et al. [12] and Daniel E.B et al. [13]. From experimental data measured by Sheikh A. Rezan et al. [5,14], the reduction mechanism of TiO_2 by H_2 follows a shrinking core model. Details on the shrinking core model used was explained elsewhere [8,12]. The kinetic model was setup using MATLAB R2011b software. In order to solve the complicated equations regarding H_2 reduction of TiO_2 in the kinetic model, step by step modeling process was done based on its mass and thermal transport coefficients together with its thermo-physical quantities [5]. The kinetic model developed in this study has been successfully applied previously on isothermal and non-isothermal reduction of Fe_2O_3 in H_2 gas atmosphere [15,16].

Determination Rate of Transfer

Consider the chemical reaction in Eq. 1. TiO_2 was a solid reactant metallic oxide compound (spherical pellet), H_2 was the reactant gas, Ti_2O_3 was the solid reaction product and H_2O was the evolved gaseous product. If gaseous transport away from the

pellet was defined to be positive, the rates of mass transport for n_A (H_2) and n_B (H_2O) for ideal gas behavior was represented by Eq. 3 and 4.

$$n_A = \frac{4\pi Ro^2}{R} K_m \left(\frac{PH_2(s)}{Ts} - \frac{PH_2(o)}{Tg}\right) \quad (3)$$

$$n_B = \frac{4\pi Ro^2}{R} K_m \left(\frac{PH_2O(s)}{Ts} - \frac{PH_2O(o)}{Tg}\right) \quad (4)$$

where K_m= mass transfer coefficient, R= gas constant of 82.05 atm. cm^3/g-mole-K) $P_A(a)$ = pressure of reactant gas in atmosphere, $P_B(a)$ = pressure of product gas in atmosphere and a= surface (s) or bulk (o) gas.

Prediction of Convective Mass Transfer Coefficients

The convective mass transfer coefficient between a gas and a sphere was calculated from Eq. (5),

$$\mathbf{Sh} = \mathbf{2.0} + (\mathbf{Re})^{\frac{1}{2}}(\mathbf{Sc})^{\frac{1}{3}} \quad (5)$$

$$Sh = \frac{K_m \times d_o}{D_{AB}} \quad (6)$$

where Sherwood number (*Sh)* is a function of the mass Reynolds number (Re), Schmidt number (Sc), and binary diffusivity (D_{AB}). AB was the reductant and product gas defined as H_2-H_2O.

Prediction of Binary Diffusivity

The calculation method was based on kinetic theory and gives predictions with an average deviation of 4 pct. (%) with a maximum deviation of 16% [15]. The binary diffusivity b_{AB} prediction was made using Eq. 7.

$$\beta_{AB} = \frac{BT^{3/2}\sqrt{(\frac{1}{M_1} + \frac{1}{M_2})}}{\mathrm{P} * \mathrm{r}(r_{AB})^2 \times ID} \quad (7)$$

where r_{AB} = collision diameter (Å), taken as the mean of the collision diameters of components A and B, M_1, M_2 = molecular weights of components H_2 and H_2O, $B=[10.7-2.46\sqrt{(1/M_A+1/M_B)}]\times10^{-4}$, ID= Collision integral of diffusion, P = absolute pressure (atm.) and T = Temperature (K).

Prediction of Convective Heat Transfer Coefficients

Eqs. 8 and 9 below enables accurate prediction of the convective heat transfer coefficient between a sphere and flowing gas using dimensionless parameter called Nusselt (Nu) number.

$$Nu = 2.0 + 0.6(Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}} \quad (8)$$

$$Nu = \frac{h_c \times d_o}{K_f} \quad (9)$$

where Re =Reynolds number, Pr = Prandtl number, h_c = convective heat transfer coefficient and K_f = thermal conductivity of the H_2 gas film.

Determination Rate of Reaction

The location of the reaction interface determines reaction points E and F along the spherical pellet in Eq. 10. These points enable the calculation of R′ (% Reduction). This, along with bulk gas composition, evaluation of transport mass coefficients, and the temperatures of the reaction interface and gas stream enables calculations of the instantaneous reaction rate (n_C) at any time during the reaction.

$$n_C = \frac{(P_B(o) - K_{eq} * P_A(o))}{T_g * (K_{eq}\left(\frac{E}{D_A,eff} + \frac{F}{K_{mA}}\right) + \left(\frac{E}{D_B,eff} + \frac{F}{K_{mB}}\right)} \quad (10)$$

where $E = R^*(R_o\text{-}r_i)/[4\pi(r_i \times R_o)]$ and $F = R/4\pi Ro^2$ are location points of reaction interface on the sphere, mass transfer coefficient of molecules A and B for gases (K_{mA}, K_{mB}) $D_{A,eff}$ and $D_{B,eff}$ are the effective Knudsen diffusion for molecules A and B.

Determination of Pellet Temperature

Prediction of the variation of pellet temperature during reaction was more difficult than the determination of the gaseous mass transport rate. This was due heat transfer at the reactant core that occurs simultaneously with heat transfer through the accumulated solid reaction product and the bulk gas. An assumption was made that the accumulation of heat in reaction zone was zero. With this assumption, an average pellet core temperature of T_C was defined to account for the overall heat transfer away the pellet. This was given in Eqs. 11-14.

$$T_C = \frac{\Delta t\left(n_B * C_{pH2O}(T_C) * (T_C - T_o) + n_A C_{pA}(T_p) * (T_p - T_o) - \frac{4\pi K_p r_i R_o}{(R_o - r_i)} * T_s\right) + T_{C_{z-1}} * \frac{4}{3}\pi r i^3 * C_{pC}(T_C) * \rho_c + 4\pi r_i^2 \Delta r * \rho_c * (-\Delta H(T_C))}{4/3\pi r_i^3 * C_{pC}(T_C) - \frac{4\pi K_p R_o r_i}{(R_o - r_i)} * \Delta t} \quad (11)$$

$$T_p = T_C - \frac{R_o}{(r_i + R_o)} \times (T_C - T_S) \quad (12)$$

$$T_S = \frac{\begin{array}{c} n_A[C_{pA}(T_P) * (T_P - T_o) - C_{pA}(T_g) * (T_P - T_o)] \\ +n_B[C_{pB}(T_C) * (T_C - T_o) - C_{pB}(T_P) * (T_P - T_o)] \\ +4\pi R_o^2 \varepsilon\alpha T_o^4 - \frac{4}{3}\frac{\pi(R_o^3 - r_i^3) C_{PP} * (T_P)}{\Delta t}\rho_P * (T_P - T_{P_{z-1}}) \\ + \frac{4\pi K_p r_i R_o}{(R_o - r_i)} * T_C + 4\pi R_o^2 h_c * T_g \end{array}}{\frac{4\pi K_p r_i R_o}{(R_o - r_i)} + 4\pi R_o^2 hc + (4\pi R_o^2 \varepsilon\alpha * T_{S_{z-1}}^3)} \quad (13)$$

$$T_g = \frac{\begin{array}{c} n_A C_{pA}(T_g) * (T_g - T_o) + GC_{pg}(T_o) * T_o + (4\pi R_o^2 h_c * T_S) \\ + 4\pi R_o^2 \alpha\varepsilon(T_S^4 - T_o^4) + n_B C_{pB}(T_P) * (T_P - T_o) \end{array}}{GC_{pg}(T_o) + 4\pi R_o^2 h_c} \quad (14)$$

where C_{pp}= heat capacity of solid product (calorie/mole.^{o}K), C_{pC}= heat capacity of solid reactant core (calorie/mole.^{o}K), C_{pg}= heat capacity of reducing gas (calorie/mole.^{o}K).

The overall reaction rate for the system represented by Eq. 2 from shrinking core model [17] can be predicted by the simultaneous solution of Eq. 10-14 done in MATLAB. Details of this solution was given elsewhere [8,11]. Lastly, after reaction rate (n_C) and time (t) of reaction have been determined, the R′ can be calculated based on Eq. 15:

$$R_o\rho_c = [1 - (1 - R')^{1/3}] = kt \quad (15)$$

where Δt = change in time of reaction = $t_2 - t_1 = -4\pi r_i \rho_c \frac{(r_2 - r_1)}{n_c}$,

R'=% Reduction (100*instantaneous weight of pellet/ initial weight of pellet sphere) = $(M_o - M_{(t)})/(M_o - M_f)$, ρ_C = molar density, M_o = initial weight of pellet (TiO_2), $M_{(t)}$ = weight of pellet at time t (Ti_2O_3 + Ti_3O_5), M_f = final weight of pellet (Ti_2O_3) and k = kinetic constant (s^{-1}).

RESULTS AND DISCUSSION

Predicted transport-limited reduction rate was derived from kinetic model by solving the numerical equations with MATLAB software. Experimentally measured rate was the reduction rate from experiments. Figure 1 below shows the experimental and

simulated data for isothermal reduction with respect to temperature and time. The highest R′ of 100% was obtained at 1773 K after 5 minutes. The experimental data at 1773 K showed R' was only 70% after 40 minutes. The low R′ for experimental data was attributed to limitations in the kinetic model. Among the limitations of the shrinking core kinetic model developed, changes in the porosity of the pellet during reduction were assumed to be constant. In actual experimental conditions, porosity change in the spherical pellet had a significant effect on the overall kinetics of the reaction. For example, effect diffusion through porous structure was much slower compared to fully dense sample. Studies by Wood, J. et al. [18] have shown that porosity change during oxidation reactions effect significantly the overall kinetics and must be taken into account.

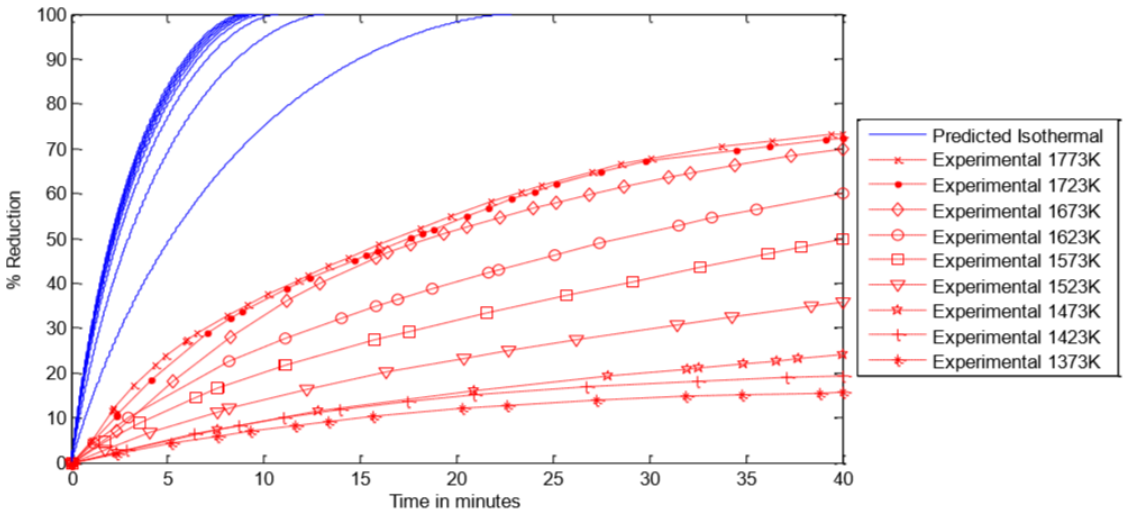

Figure 1: Comparison of predicted and experimental transport-limited reduction rate at different temperatures

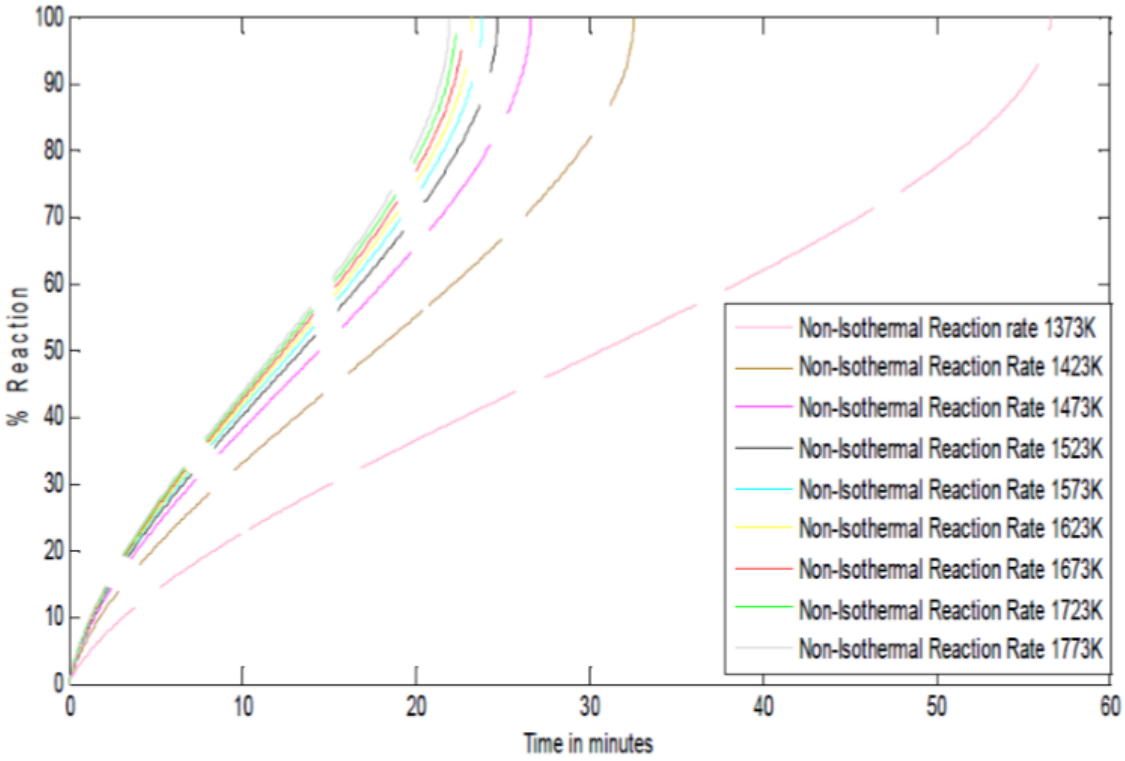

Figure 2: Predicted non-isothermal transport-limited reaction rate at different temperatures

Figure 2 shows the non-isothermal reduction with respect to temperature and time. The % Reaction was defined as $[1-(1-R')^{1/3}]$. The highest % Reaction of 100% was obtained at 1773 K after 20 minutes. Non-isothermal reduction showed a better fit to the experimental data in Figure 1 compared to isothermal reduction. The explanation for this better match was due to the mechanism of reduction. During H_2 reduction, the temperatures inside the spherical TiO_2 particles were not constant and varied according to gas concentration, location and time. The non-uniformity of the temperature in the particles was one of the reasons for the mismatch between experimental and simulated data. By accounting for this non-isothermal temperature condition by equations (11)-(14) in the kinetic model, a better match between experimental and simulated data was obtained.

CONCLUSION

Although the experimentally observed reaction rate was significantly slower than the predicted transport-limited rate, the kinetic model had indicated a good trend of similarity between experimentally observed H_2 reductions of TiO_2 with the kinetic model. The kinetic model also has provided an optimal fitting trend for the

experimental results. Furthermore, the kinetic model is a good starting point to understand the mechanism of reduction in TiO_2 when changes in the initial state were undertaken. With this kinetic model, simulated data at different fixed porosity, particle shapes, gas concentration, gas flow-rate and gas viscosity was possible. This in turn optimizes experimental time and cost in investigating kinetic effects during H_2 reduction of TiO_2. Further improvement of the kinetics model was expected by incorporating better solutions to porosity modeling inside the spherical pellet during shrinking core process.

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NOMENCLATURE

A	reactant solid
B	reactant gas
C	product solid
Cp_A	Heat capacity of gas reactant (calorie/mole.^oK)
Cp_B	Heat capacity of gas product (calorie/ mole.^oK)
D	product gas
Eq.	Equation
G	mass flow rate (gram/cm^2.sec)
K_{eq}	Equilibrium constant
R'	Percent of reduction
R_o	Initial radius (cm)
R	Final radius (cm)
T_g	Gas temperature (^oK)
T_o	Initial temperature (^oK)
T_s	Surface pellet temperature
atm	Atmosphere
d_o	Sphere diameter
r_i	Position of reaction interface (cm)
t	time

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