REDUCTION KINETICS OF TiO$_2$ POWDER COATED WITH HYDROCARBONS

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Abstract

The kinetics of the carbothermic reduction of titanium dioxide coated with hydrocarbons was investigated. The thermally programmed reduction was carried using two approaches: 1. Measuring the change of pressure of the emitted gases during heating of the sample and 2. Differential thermal analysis. It was shown that the reduction passes through four stages. The activation energies were calculated using the Kissinger method.

Key words: carbothermic reduction, coated powder, titanium oxide

INTRODUCTION

The selection of materials plays an important role in the progress of science, technology and human society. Searching for new materials that are cost and energy efficient, and also environmentally friendly, is increasing and this tendency will continue. A special attention is paid to the development of new production technologies that are low cost and use predominantly local resources like raw .materials and technological equipment.

In recent years carbide synthesis by reduction of refractory metals'oxides with gaseous hydrocarbons is of interest in science research and is intensively investigated in the most advanced countries [1,2]. These studies have described the synthesis of tungsten and titanium carbides based on carbothermic reduction with precursor (initial substance), obtained by coating tungsten trioxide (WO$_3$) or titanium dioxide (TiO$_2$) with carbon received by thermal decomposition of gaseous hydrocarbon (C$_3$H$_6$). This method improved the distribution of carbon on the surface of tungsten or titanium oxide and also it insured prevention of agglomeration of the particles. Purer product is obtained as a result and the reaction is fully finished. An essential disadvantage of the listed technologies is the use of hydrogen and gaseous hydrocarbons which produce a risk of explosion.

The aim of this study is investigation of the kinetics of the carbothermic reduction and carbide formation of TiO$_2$ coated with hydrocarbons. The layer of hydrocarbons is obtained by thermal destruction of a polyvinyl alcohol (PVA) precursor.

EXPERIMENTAL PROCEDURE

Precursor Preparation

Precursor preparation consists from the following steps: Well defined quantity of PVA (in this case 50 g.) was dissolved in distilled water. Then 5 g of titanium dioxide was added to the aqueous solution. It was stirred intensively to obtain an emulsion which was coagulated in acetone [3]. The coagulum was shredded, dried and thermally destoyed in an

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inert environment (argon). The DTA graph, the temperature regime and the concentration of the obtained carbon are presented in Figs.1 and 2. To protect the vacuum system of the equipment, the precursor was additionally heated at 873 K for 30 min.
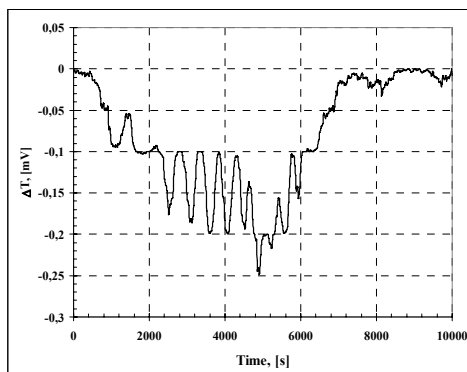

Fig.1. DTA of 50 g PVA + 5 g TiO_2 thermal destruction obtained by using the apparatus for polymers' destruction (Ar flow - 7.5 nl/h; heating rate - 5ºC/min, C = 43 wt.%).
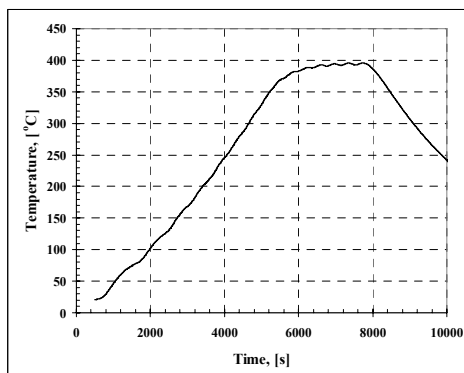

Fig.2. Temperature regime of 50 g PVA + 5 g TiO_2 destruction, obtained by using the apparatus for polymers destruction (Ar flow – 7.5 nl/h; heating rate - 5ºC/min).

Method and equipment

The method of temperature-programmed reduction (TPR) was used to study the kinetics of the carbothermic reduction of TiO_2. Theory and applications of the TPR technique have been comprehensively reviewed by Hurst et al. [5] and Lemaitre [6]. Methods for extraction of activation energies with the use of other thermoanalytical techniques (DTA, TPD, etc.) have been adapted to TPR studies. Kissinger [7] and Friedman [8] methods were introduced to TPR studies by Knözinger [9], Wimmers et al. [10] and Tarfaoui [11].

Present studies were carried out using two procedures: 1. Measuring the change of the pressure of the emitted gases during heating of the precursor (C_xH_y, CO and CO_2) and 2. Differential thermal analysis (DTA). Four heating rates were used. The precursor was placed in alumina ladles and then into a vacuum tight ceramic tube. The whole assembly

was heated in a tubular furnace under vacuum, monitored by the computerized Pirani set up (initial vacuum was ~5x10^{-4} mm Hg).

The differential thermal analysis was carried out by SETARAM Micro ATD M-5-(France) in helium at different heating rates. The sample with approximate weight ~ 0.03 g was placed in corundum crucible and heated up to 1723 K. The temperature, T, and ΔT signals were registered by Voltcraft'96 and MS 8218 multimeters. The X-ray analyses were carried out by Philips X'Pert Pro device using Cu cathode. The qualitative phase analysis was realized from XRD pattern by X´Pert High Score program using PDF 2 (Powder Diffraction File).

RESULTS AND DISCUSSION

The thermodynamic calculations (performed by the Montreal Polytechnic program www.crct.polymtl.ca) showed that the carbothermic reduction is predominant up to 1103ºC according to reaction (1),

$$TiO_2 + 2C \rightarrow TiC + CO_2, \tag{1}$$

and above this temperature according to reaction (2)

$$TiO_2 + 3C \rightarrow TiC + CO, \tag{2}$$

The equilibrium constant for each reaction is presented in Fig.3. It was also confirmed by the study [4]. The reaction (2) went through formation of inferior titanium oxides. The following reactions were possible according to the Gibs` free energy:
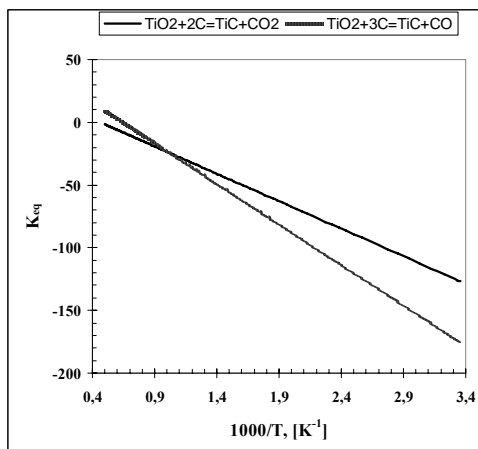
$$4TiO_2 + C \rightarrow Ti_4O_7 + CO(g) \tag{3}$$
$$3\,Ti_4O_7 + C \rightarrow 4Ti_3O_5 + CO(g) \tag{4}$$
$$Ti_3O_5 + 8C \rightarrow 3TiC + 5CO(g) \tag{5}$$

Fig.3. The dependence of the reaction equilibrium constants on temperature for $TiO_2 + C$ system.

Differential Thermal Analysis

The differential thermal analysis (DTA) was carried out at five different heating rates: 4.6, 6.6, 9.4, 11 and 14 K/min. The recorded DTA graphs are presented in Fig.4. The temperatures, where they had local extremum T_{max}, were determined (Table 1). They were calculated according to the Kissinger model, equation (6), and the values of the activation

energies - by the angle coefficient of the lines (Fig.5), also presented in Table 1, where β is heating rate, E - activation energy and R - gas constant.

$$\frac{E}{RT_{max}^2} = \frac{A}{\beta} \exp\left(-\frac{E}{RT_{max}}\right)\left(-\frac{df(\alpha)}{d\alpha}\right)_{T=T_{max}}$$

(6)

Tab.1. Heating rate, β, maximum temperature, T_{max}, activation energy, E, and correlation coefficient, r, for the carbothermal reduction of titanium dioxide coated with hydrocarbons. DTA experiment.

Heating rate β [K/min]	I. peak from right to left T_{max} [K]	II. peak from right to left T_{max} [K]	III. peak from right to left T_{max} [K]
4.6	1562	1480	1386
6.6	1596	1487	1398
9.4	1646	-	-
11	1647	1508	1469
14	-	1522	1471
E [kJ/mol]	E=172.2; $r^2 = 0.9657$	E=454.7; $r^2 = 0.9677$	E=157.8; $r^2 = 0.9133$

The value obtained for the total activation energy E_{sum} = 784.7 kJ/mol was in good correlation with the value of 731.6 kJ/mol, obtained by G. A. Swift and R. Koc [2].
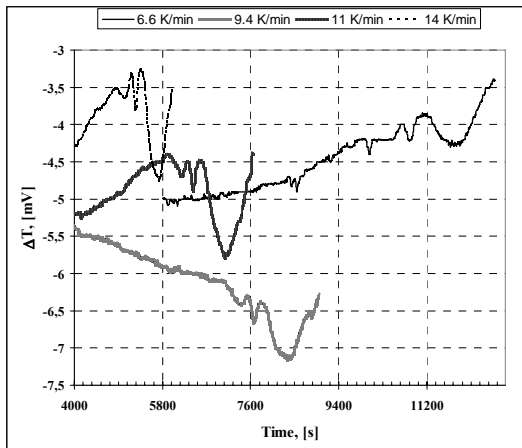

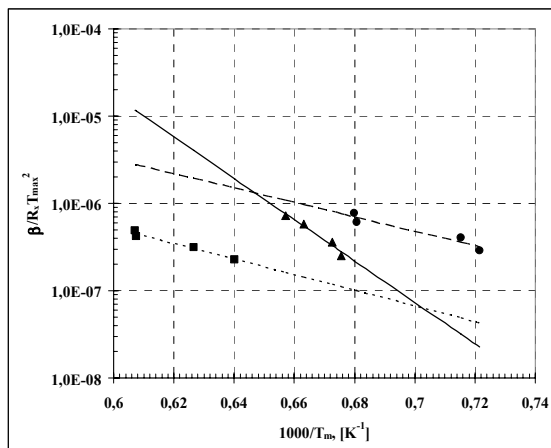Fig.4. DTA graphs for experiments with hydrocarbon coated TiO_2 powder, carried at different heating rates.

Fig.5. Kissinger plot, β/RT^2_{max} vs. $1000/T_{max}$, of the data obtained by the DTA experiments: ■ – data for the I. peak from right to left, ▲ - data for the II. peak from right to left, ● - data for the III. peak from right to left.

Kinetic examinations

Figure 6 shows the graphs of the total pressure change of the emitted gases during heating. The heating of TiO_2 coated by hydrocarbons was carried out with 4 different speeds: $\beta = 4.8, 7.2, 9.3$ and 11.3 K/min. Three peaks clearly evident on the graphs corresponded to the three different processes taking place during the precursor heating. At first the water evaporated, and then the final decomposition of the hydrocarbon took place which finished by 1273 K, depending on the heating rate. After that a gradual increase of the pressure of the emitted gases started because of the reactions (3) – (5). In this stage the pressure went through three different stages corresponding to the above mentioned chemical reactions. This became clearer when the DTA graph at 6.6 K/min was compared to the pressure change of the emitted gases at nearly the same heating rate 7.2 K/min, Fig.7. The temperatures were determined by the kinetic curves where the peak, corresponding to the final destruction of the hydrocarbon, had a maximum and these data are listed in Table 2. The data were processed by the least squares method according to the Kissinger equation and by the angle coefficient of the obtained line, Fig.8, and the calculated activation energy is presented in Table 2.

Tab.2. Heating rate, β, maximum temperature, T_{max}, calculated activation energy, E, and correlation coefficient, r, for the carbothermal reduction of titanium dioxide coated with hydrocarbons. Pressure experiment.

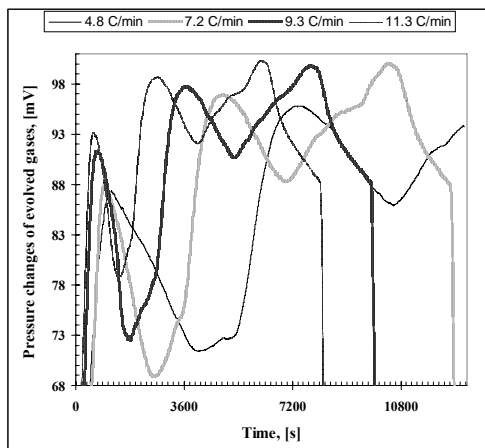| Heating rate β [K/min]	T_{max} [K]
4.8	976.5
7.2	981.4
9.3	1009.5
11.3	1011.9
E = 135.4 kJ; r^2=0.8193	

Fig.6. The dependence of the total pressure of the emitted gases during the carbothermic reduction of TiO_2 coated with hydrocarbons on time. Reduction temperature = 1673 K, different heating rates.
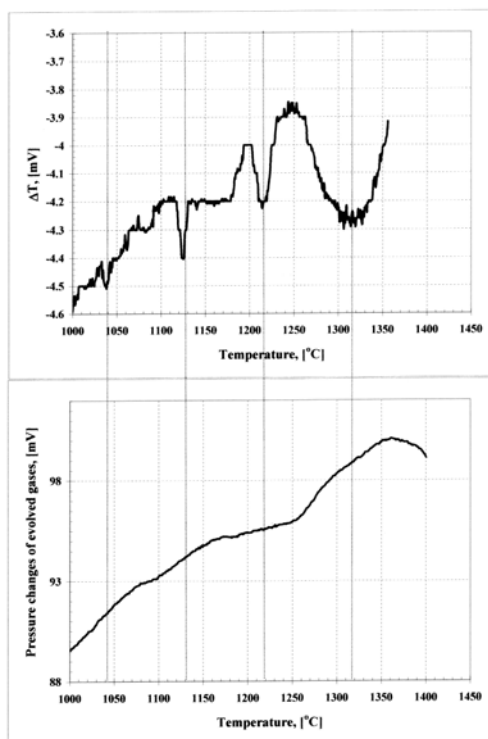

Fig.7. Graphs showing the existence of four stages at carbothermic reduction of TiO_2 powder, coated with hydrocarbons. Above, the DTA experiment (heating rate 6.6 K/min). Below, the pressure change experiment carried at nearly the same heating rate 7.2 K/min.
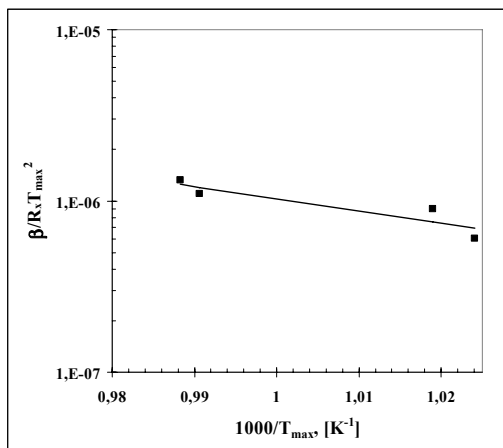
Fig.8. Kissinger plot, β/RT^2_{max} vs. $1000/T_{max}$, of the data presented in Table 2 for TiO_2 coated with hydrocarbons.

X-ray structural analysis

      X-ray graph of a sample, obtained during the kinetics study of carbothermic reduction of TiO_2 coated with hydrocarbons, is shown in Fig.9. It is seen that TiO_2 coated with hydrocarbons is fully transformed into TiC at 1673 K after 30 min, even at heating rate of 11.3 K/min. Only the X-ray patterns of TiC are visible in the X-ray graph (Fig.9).
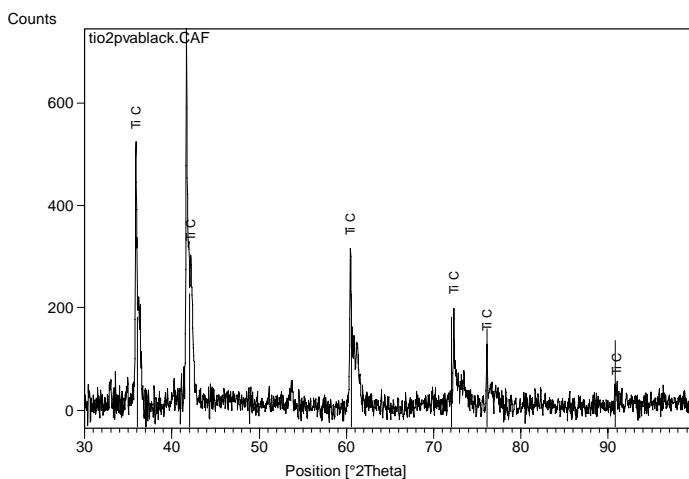

Fig.9. X-ray qualitative phase analysis of TiC, obtained by carbothermic reduction of TiO_2, coated with hydrocarbons, at 1673 K for 30 min (heating rate 11.3 K/min).

CONCLUSIONS

A study of kinetics of the carbothermic reduction of titanium dioxide coated with hydrocarbons by two different methods (change of the pressure of the emitted gases during sample heating and differential thermal analysis) was made. The following conclusions could be drawn:

- the carbothermic reduction of TiO_2 coated with hydrocarbons passes through four clearly defined stages;
- the activation energies for each stage were derived. The activation energy determined, $E_{sum} = 784.7$ kJ/mol, is in good correlation with the value of 731.6 kJ/mol, obtained by G. A. Swift and R. Koc [2];
- it is shown that the carbothermic reduction of TiO_2 coated with hydrocarbons, carried at 1673K for 30 min, leads to full transformation into TiC.

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