Oxidation Kinetics Studies of $Ti_3C_2T_x$ MXene using Freeman-Carroll Method

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Abstract

$Ti_3C_2T_x$ MXene is synthesized from $Ti_3Al_2C_3$ MAX phase by using HF treatment and characterized by X-ray diffraction In addition, oxidation of $Ti_3C_2T_x$ MXene in nitrogen environments from room temperature to 500 °C is studied by thermogravimetric analysis. The experiment shows that oxidation of $Ti_3C_2T_x$ MXene starts at 275 °C. Activation energy of oxidation of $Ti_3C_2T_x$ MXene is determined using the Freeman Carroll method. It is found that in a nitrogen environment and in a strong oxidation temperature range, oxidation activation energy of $Ti_3C_2T_x$ MXene is approximately 235.6 kJ mol^{-1}.

Keywords: $Ti_3C_2T_x$ MXene, Kinetics, Oxidation activation energy, Freeman Carrol method.
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Introduction

$Ti_3C_2T_x$ MXene is a two-dimensional transition metal carbide whose stability and performance in a variety of applications, including energy storage, catalysis, and sensing etc, may be understood by studying its oxidation kinetics [1-4]. This oxidation kinetics can be understood using Freeman - Carroll method [5], which utilizes the relation between temperature, time and the rate of reaction. This method analyses non-isothermal kinetic data, particularly when the reaction rate is temperature dependent. Thus, order to understand the stability of $Ti_3C_2T_x$ MXene, in this paper, we reported the oxidation behavior of $Ti_3C_2T_x$ MXene at high temperatures in nitrogen environment.

Experimental Method

$Ti_3C_2T_x$ MXene Preparation

An amount of 1 gm Titanium Aluminum Carbide $Ti_3Al_2C_3$ MAX phase (90.00% pure) ≤ 100µm Particle size was added in concentrated Hydrofluoric acid HF (40%) of Sigma Aldrich solution and stirred for 26 hours at room temperature. The solution then filtered and washed frequently with distilled water and ethanol until the pH of solution became neutral. Powder obtained after filtration was dried in the oven for 8 hours.

$Ti_3C_2T_x$ MXene characterization

The power was further investigated for its structural properties using Bruker D8 Advance CuKα (lambda = 0.15408 nm) diffractometer in the range 10°-80°. Thermogravimetric analysis of the powder was carried out using Model No.-TGA55 Make - TA Instruments. USA. The $Ti_3C_2T_x$ MXene powder sample was placed in the alumina crucible of the TG Analyzer. Its temperature was increased from room temperature to 500 °C with a heating rate of 20 °C /min in the presence of a nitrogen environment.

Results and Discussion

X-ray analysis

Figure 1. shows the XRD pattern of the powder obtained by etching Ti3Al2C3 MAX phase by HF at room temperature. The diffraction peaks at 2θ viz: 18.80°, 38.76°, 41.57°, shows the pure phase formation of $Ti_3C_2T_x$ MXene matches with previously reported results [4].

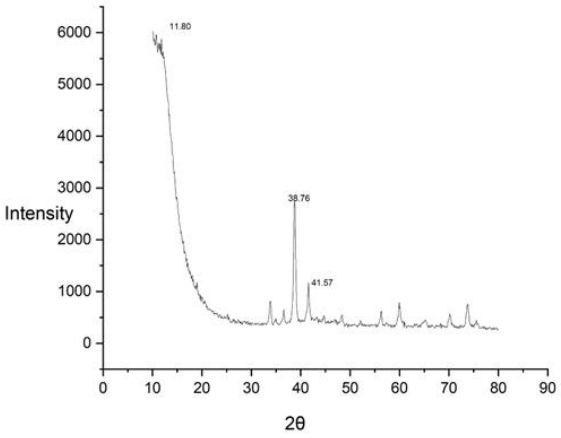

Figure 1: XRD plot of $Ti_3C_2T_x$ MXene.

Thermogravimetric analysis: Oxidation experiments

Figure 2 shows the TGA plot of $Ti_3C_2T_x$ MXene in the nitrogen environment with a heating rate of 20 °C/min. From the TGA plot, it is seen that the oxidation of $Ti_3C_2T_x$ MXene starts at 275 °C and continues rapidly peaking upto 400 °C. This indicates the onset of decomposition of $Ti_3C_2T_x$ Mxene which leads to the incorporation of oxygen forming TiO_2. Further mass decreases after 400 °C which might be due to the decomposition and evaluation of CO_2 through the sample. This indicates that oxidation of $Ti_3C_2T_x$ MXene is a solid-gas reaction.

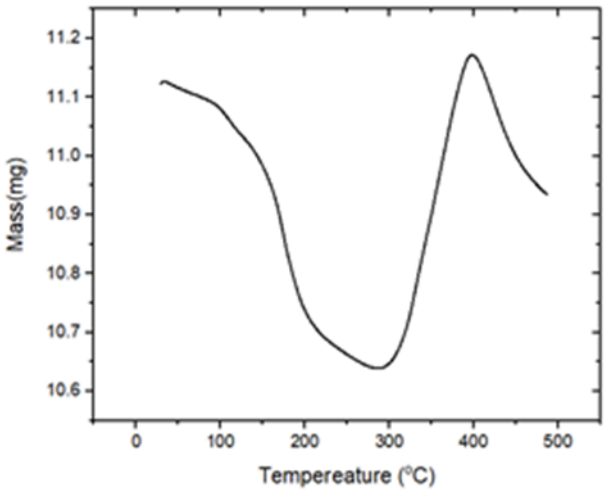

Figure 3: TGA Plot of $Ti_3C_2T_x$ MXene.

Figure 3 shows the plot of the derivative of mass with temperature. From the figure, it is seen that the rate of mass change is rapid after the onset of oxidation; it remains constant from 320 °C to 360 °C and rate decreases very rapidly after 360 °C. This indicates the complete oxidation of $Ti_3C_2T_x$ MXene sample.

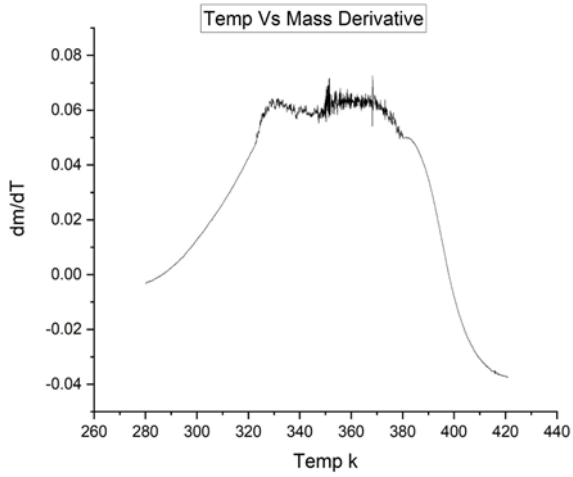

Figure 3: Weight gain plot TGA plot of $Ti_3C_2T_x$ MXene

Freeman Carrol method

The activation energy decides the oxidation stability of $Ti_3C_2T_x$ MXene and it depends on the rate of the reaction.

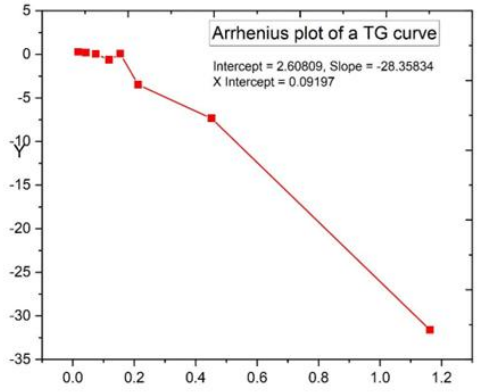

Figure 4: Arrhenius plot of a TG curve plot TGA Plot of $Ti_3C_2T_x$ MXene

Large value of activation energy indicates the smaller reaction rate and vice versa. Now, we will utilize the Freeman Carroll method and standard Arrhenius equation (1) to obtain the oxidation activation energy.

$$\frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)^n \qquad \ldots (1)$$

Figure 4 shows the Arrhenius graph obtained from thermogravimetric analysis of $Ti_3C_2T_x$ MXene. The data obtained from terms given below,

$$\frac{\Delta \ln\left(\frac{dm}{dt}\right)}{\Delta \ln\left(m_\infty - m_t\right)} \quad and$$

$$\frac{\Delta\left(\frac{1}{T}\right)}{\Delta \ln\left(m_\infty - m_t\right)}$$

were plotted considering m_∞ is mass when complete oxidation of the sample takes place. From the slope of the line activation energy of oxidation of $Ti_3C_2T_x$ MXene is approximately 235.6 kJ mol^{-1} and the intercept indicates that order of reaction is 2.6. This indicates the need for a controlled and inert atmosphere to avoid the oxidation of $Ti_3C_2T_x$ MXene.

Conclusion and Future Perspective

The experiment and estimated results suggest that the oxidation of $Ti_3C_2T_x$ MXene in a nitrogen environment takes place above 275 °C. Its oxidation activation energy is found to be approximately 235.6 kJ mol^{-1}. Thus, to control the oxidation under heat treatments inert atmosphere should be maintained. In this regard more insights will be further obtained when this material will be investigated under different gaseous environments and heating rates.

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