Kinetic studies of isothermal decomposition of \((\text{NH}_4)_4\text{UO}_2\)\((\text{CO}_3)_3\) to uranium oxide

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Abstract

The ammonium uranyl carbonate, \((\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3\), is an important material used in \(\text{UO}_2\) and \(\text{U}_3\text{O}_8\) ceramics production for the nuclear fuel fabrication. Thermal study and kinetic analysis of ammonium uranyl carbonate conversion under isothermal conditions has been studied in air atmosphere to obtain the tri-uranium octoxide \((\text{U}_3\text{O}_8)\), using muffle furnace equipment, UV–visible spectrophotometer, gas adsorption, Hg porosimetry, laser granulometry, and optic spectroscopy. The textural properties (specific surface area, morphology, pore size, grain size, inter-particular porosity, and intra-particular porosity) and characteristics (uranium content and stoichiometry) of the prepared samples were estimated from the physical–chemical characterization. The kinetic parameters were estimated by a fitting of the experimental data. The activation energy \(E_a\), frequency factor \(A\), and reaction rate constants \(k\) were calculated from the conventional and iso-conversion kinetic models and were within the range of literature values. The activation energy average values are 36.69 and 30.36 kJ mol\(^{-1}\) by conventional and iso-conversion models, respectively.

Keywords

Carbonate uranyl ammonium, uranium oxide, isothermal analysis, kinetic parameters, modeling

Introduction

This article is an extension of a previous paper where the ammonium uranyl carbonate (AUC) samples under non-isothermal conditions were decomposed and characterized.\(^1\)
Using modeling approach and under isothermal conditions, the kinetic parameters of the solid-state reactions (activation energy $E_a$, rate constant $k$, and pre-exponential factor $A$) can be obtained.\textsuperscript{2–4}

The uranium oxide (UO$_2$) is used as nuclear fuel in the nuclear fuel cycle. This choice is due to the chemical and physical properties of the UO$_2$ at high temperature.

The characteristics of a UO$_2$ and U$_3$O$_8$ powder influence the final properties of the UO$_2$ sintered pellets.\textsuperscript{5–7}

The irradiation behavior and the performance of the nuclear fuel are influenced by the characteristics and properties of the U$_3$O$_8$ powders and UO$_2$ pellets.

The AUC is used in the production of UO$_2$ powders destined for UO$_2$ pellet fabrication of nuclear fuel. The ignition process of the AUC powder is one of the solid-state reaction mechanism involved in the nuclear fuel process.

The AUC powder precipitates from the uranyl nitrate solution or can be also precipitate in amine salt extraction from a uranyl sulfate solution. The UO$_2$ powder resulting from these two ways will have different textural and structural properties.

In addition, the AUC decomposition conditions during the ignition process influence the U$_3$O$_8$ powder properties and the UO$_2$ pressing and sintering processes.

The ignition process of the AUC occurs with a great evolution of gases (CO$_2$ and NH$_3$). The porosity and the pore structure of the products UO$_3$ or U$_3$O$_8$ obtained after the decomposition of the AUC are conditioned by the form in which the gases CO$_2$ and NH$_3$ evolved. The porosity resulted from the AUC thermal decomposition will condition the sintering and the in-pile behaviors of UO$_2$ pellets.

The AUC decomposition can be presented in the following reaction\textsuperscript{1}

$$3(NH_4)4UO_2(CO_3)_3U_3O_8 + 12NH_3 + 9CO_2 + 6H_2O + \frac{1}{2}O_2$$

Several authors have studied the decomposition of uranyl carbonate or ammonium uranyl compounds. In our previous study, we gave a detailed description of previous work cited in literature on the isothermal and non-isothermal decomposition of AUC.\textsuperscript{8–14}

In this work, isothermal decomposition of AUC compound has been examined using several characterization techniques. The purpose of this study is to carry out the uranium oxide powder characterization obtained from the isothermal decomposition of the AUC. Once the AUC is decomposed to U$_3$O$_8$ powder in air atmosphere, the textural properties of the intermediate and U$_3$O$_8$ phases have been studied by using UV–Visible spectrophotometer, gas adsorption (Barrett, Joyner and Halenda and Brunauer, Emmett and Teller), mercury porosimeter, laser granulometry, and optic spectroscopy methods. The effect of the ignition process is discussed in terms of the inter-granular porosity of the powder as measured by mercury intrusion porosimetry. The values of the kinetic parameters (activation energy $E_a$, reaction rate constants $k$ and frequency factor $A$) were calculated by model-fitting (conventional method) and model-free (iso-conversional) methods.

**Kinetic modeling**

**Modeling approach**

Kinetic studies of different uranyl compounds have been investigated by many researchers. Different models can be employed to study the kinetics of uranyl compound decomposition,
which include nucleation models, geometrical contraction models, diffusion models, and reaction order models. These models of kinetic expressions have been employed to represent the kinetic of the solid-state reaction.3,4,5,15,16

Table 1 presents the summary of the various kinetic expressions used in our study, to treat the isothermal kinetics of the AUC decomposition.2,16

The resulting kinetic parameters of the AUC ignition process, from the application of various model equations, are used to interpret the reaction mechanism. The variation of activation energy \( E_a \) with conversion fraction \( \alpha \) indicates the nature of steps involved in reaction mechanism of the AUC ignition process.

**Isothermal kinetic methods**

Two methods are used to analyze the isothermal kinetic data: the model-free (iso-conversional) methods and the model-fitting (conventional) methods.

**Model-free/standard iso-conversional methods.** Model-free methods calculate the reaction activation energy \( E_a \) without suppositions.

This method can be derived from equation (1)2,3,4

\[
g(\alpha) = A e^{-\frac{E_a}{RT}} t
\]

Linearization of equation (1) gives

\[
\ln g(\alpha) = \ln\left(\frac{A - E_a}{RT}\right) + \ln t
\]

Equation (2) can be reorganized to give

\[
-\ln t = \ln\left(\frac{A}{g(\alpha)}\right) - \frac{E_a}{RT}
\]

A plot of \(-\ln t \) versus \(1/T\) for each \( \alpha \) gives \( E_a \) from the slope of that equation for that \( \alpha \) and the pre-exponential factor \( A \) without model fitting.
More details about the calculation method of conversion fraction \((\alpha)\), rate of a solid-state decomposition reaction \((d\alpha/dt)\), and integral mathematical expression for the mechanism reactions \(g(\alpha)\) have been shown elsewhere.\(^1\)

**Isothermal model-fitting methods (conventional method).** In order to analyze the isothermal kinetic data from the conventional method, two fits are involved:

The first determines the rate constant \((k)\) of the model that best fits the data according to equation (4)

\[
g(\alpha) = kt \tag{4}\]

The second fit determines kinetic parameters \(E_a\) and \(A\) using equation (5)\(^2,3,4,16\)

\[
k = Ae^{-\frac{E_a}{RT}} \tag{5}\]

The slope from this second fit gives the reaction rate constant \((k)\), and this fitting is repeated at each temperature. According to the Arrhenius equation, the rate constants are used for the second fit for each model (Table 1). The pre-exponential factor and activation energy are obtained from the intercept and slope of this plot, respectively. The obtained values of the kinetic parameters are compared with the values determined under non-isothermal conditions.\(^1\)

**Materials and methods**

The AUC commercial grade material powder was used in our study. To carry out the isothermal AUC decomposition experiments, a muffle furnace (carbolite) was used. The samples about 10 g were heated, in air atmosphere, in an open cylindrical platinum crucible of 30-mm diameter and 45-mm height. The temperatures ranging from 100°C to 900°C were selected for the experiments.

To investigate the textural properties of samples, the following methods were used: laser granulometer analyzer (Mastersizer) to measure the average and the distribution of the particle size; the BET method using ASAP surface area analyzer (Micromeritics) to measure the specific surface area; and the mercury porosimetry (Micromeritics) to measure the porosity. The method description to evaluate the \(N_2\) adsorption isotherm measurements, the evolution of porosity and specific surface area of the samples, porosity, and pore size distribution of samples has been shown elsewhere.\(^17\) The UV–visible spectrophotometer was used to calculate the stoichiometry of the obtained uranium oxide powders (O/U ratio).\(^18\) The measurements were performed in triplicate, and each result presents the mean ± standard deviation (SD).

**Results and discussion**

**Characterization of the raw and treated AUC samples**

The results of the chemical and physical characterization of the used AUC powder (Figure 1) have been given elsewhere.\(^1\)

Optic microscope photographs of the AUC and \(U_3O_8\) samples are shown in Figure 2. In this figure, it can be observed that the original AUC powder (Figure 2(a)) is presented in the
agglomerates and heterogeneous form. After the isothermal decomposition (ignition process), the AUC powder becomes more homogeneity with the spherical shape. We note that the particles of AUC powder are less agglomerated after ignition (Figure 2(b)), then the original AUC (Figure 2(a)).

The particle size and pore size distribution have an effect on the UO$_2$ and U$_3$O$_8$ powder properties. Using the principle of laser diffraction, the mean diameter of AUC and U$_3$O$_8$ samples were found to be 44 $\pm$ 2 $\mu$m and 25 $\pm$ 2 $\mu$m, respectively.

The general shape of the sample’s N$_2$ adsorption–desorption isotherms of AUC and U$_3$O$_8$ did not change, showing just an increase in the amount of nitrogen adsorbed for U$_3$O$_8$ sample. The dominant pore for AUC and U$_3$O$_8$ samples occurs in the diameter ranges from 3 to 6 nm and 4 to 25 nm, respectively. The AUC and U$_3$O$_8$ samples have pore volumes of 0.001 and 0.020 cm$^3$ g$^{-1}$, respectively. The AUC sample exhibits a narrower pore distribution; this

Figure 1. Samples of AUC and U$_3$O$_8$ powders.

Figure 2. (a) Original AUC sample and (b) U$_3$O$_8$ sample, AUC treated at 500°C.
shows that the isothermal decomposition makes the pore size distribution wider for U₃O₈ sample than AUC sample.

Results of the UV–visible spectrophotometry analysis of the final oxide confirmed that the end product of AUC ignition process under isothermal conditions at temperature value \( T = 500°C \) is tri-uranium octoxide, with \( O/U = 2.65 \pm 0.02 \) (Figure 3).

The specific surface area and pore distribution of AUC and tri-uranium octoxide samples obtained from the AUC decomposition as a function of temperature have been studied. The specific surface area, pore volume and pore diameter evolution of uranium oxide (intermediate phase), and tri-uranium octoxide as a function of temperature have also been studied. The dependence of these parameters on the isothermal decomposition temperature can be seen.

The plots of mercury penetration volume against absolute Hg intrusion pressure for the AUC and U₃O₈ samples show that the pressure up to 10 atm. represents the filling of macrovoids in the studied samples. It can be seen that the cumulative mercury intrusion volume of the AUC sample is higher than the U₃O₈ sample, indicating that isothermal treatment decreases the pore volume.

The porosity distribution results of the AUC and U₃O₈ powders, as obtained with intrusion mercury porosimetry, show the dominant pore size of 5–40 μm for AUC sample and 5–12 μm and 0.1–1 μm for U₃O₈ sample. The AUC powder is mono-modal, and the U₃O₈ powder is bi-modal. In the case of U₃O₈ powder, the first step is due to the inter-particular pores (range from 5 to 12 μm of pore size) and the second to the intra-particular pores (range from 0.1 to 1 μm of pore size). This porous structure observed during the ignition process of the AUC particle is produced by the gases generated during its decomposition.

Comparison of pore size distributions by mercury immersion between the AUC and the U₃O₈ powders shows that the intra-particular porosity appears in the U₃O₈ oxide (region from 0.1 to 1 μm). The porosity distribution of U₃O₈ is displaced to lower pore size and has lower range, indicating that the low porosity detected after decomposition of AUC sample is due to the internal porosity of the U₃O₈ powder. The observed shift of porosity
distribution toward lower pore size, in the case of the U$_3$O$_8$ sample, is produced by the breaking of the intra-particular pores of the AUC during the ignition process.

**Isothermal kinetic study**

The plots of $\alpha$ versus time for the various temperature values are presented in Figure 4. As can be seen, this figure shows that under isothermal conditions, changing the temperature does not affect the shape of the $\alpha$–time plot. The curves are sigmoidal in shape, and various regions have been defined (induction period, acceleratory period, and decay period).

**Reaction rate of AUC isothermal decomposition.** Figure 5 presents the reaction rate evolution for the isothermal decomposition of AUC powder versus the conversion rate $\alpha$ at various temperatures. We can observe, for each temperature value, that the reaction rate values passes by a maximum corresponding to a maximum conversion rate ($\alpha_m$) value, and the conversion rate values increase with the temperature, then decrease as the reaction progresses. We can note that the reaction kinetics is faster since the temperature is high.

**Evaluation of kinetic parameters using iso-conversional and conventional methods.** The kinetic parameters were determined from the isothermal curves, by using the conventional and iso-conversional (standard) methods.

**Iso-conversional method.** The activation energies $E_a$ were determined from the isothermal curves, by using the standard method. A plot of $-\ln t$ versus $1/T$ for $\alpha = 0.5$ gives the $E_a$
value from the slope for that $\alpha$. The activation energy determined at $\alpha = 0.5$ from the slope of the straight line was 40.28 kJ mol$^{-1}$.

The $E_a$ values calculated for a set of isothermal curves at 150°C, 200°C, 250°C, 300°C, 350°C, 400°C, 450°C, and 500°C for each conversion fraction $\alpha$ (0.1 $\leq$ $\alpha$ $\leq$ 0.9) are listed in Table 2.

From Table 2, it can be seen that the activation energy obtained with the iso-conversional method varies from 32.15 kJ mol$^{-1}$ ($\alpha = 0.9$) to 42.60 kJ mol$^{-1}$ ($\alpha = 0.3$). Figure 6 presents the $E_a$ values of the AUC decomposition under isothermal conditions as a function of $\alpha$. It can be seen that activation energy is dependent on conversion; the $E_a$ values lightly increase.
and then decrease with an increase in the percentage conversion. The $E_a$ variation as a function of $\alpha$ indicates that more than one reaction is occurring. This means that the reaction mechanism is not the same in the AUC decomposition during the ignition process.

Baldea et al.\textsuperscript{19} have studied the thermal decomposition of ammonium uranium fluoride in the temperature range of 250°C–500°C using the Arrhenius relation. The activation energy value 43.67 kJ mol$^{-1}$ was obtained; this value is very close to the $E_a$ value found in this present study.

Conventional model-fitting method. The $\alpha$ versus time curves at different temperatures can be obtained from the isothermal model-fitting method. Also, the $g(\alpha)$ values can be obtained from the curve for each model. From the data fit ($g(\alpha)$ vs $t$) for each model and temperature, the kinetic parameters can be calculated for each model from the second data fit (Arrhenius plot).

The choice of the kinetic equation which describes the reaction mechanism of the AUC isothermal decomposition is done after the verification of several possible kinetic equations (Table 1). The kinetic parameter data have been calculated using the conventional model-fitting method. In order to estimate the pre-exponential factor, the kinetic equation function nucleation models (P2, P3, P4, P3/2, A2, A3, and A4), geometrical contraction models (R2 and R3), diffusion models (D1, D3 and D4), and reaction order models (F1, F2, F3, and F4) were tested to simulate the isothermal decomposition mechanism of AUC (Tab. 1).

The reaction rate constants $k$ values calculated from the conventional model-fitting method (F1, A2, R3, P3/2, D1, D3, and D4 models) are summarized in Table 3. The obtained rate constant values will be used to calculate the action energy values. As summarized in Table 3, the temperature changes affect the kinetics through the rate constant, and the reaction rate increases with increasing temperature.

R2 values calculated according to the experimental values from plotting revealed that the decomposition process is an Avrami-Erofeev (A2) kinetic ($R^2 = 0.999$).
The pre-exponential factor $A$ can be obtained from the straight line using the Avrami-Erofeev A2 model (Table 1). The values of the rate constant $k$ for each temperature can be obtained by plotting the expression $(-\ln (1 - \alpha))^{1/2}$ versus time. The activation energy $E_a$ and the pre-exponential factor $A$ were obtained by plotting $\ln k(T)$ versus $1/T$. Table 4 presents the $E_a$ and $A$ values.

Model-fitting results agreed with those obtained from the Avrami-Erofeev A2 model, compared to the others models (F1, A2, R3, P 3/2, D1, D3, and D4). As Table 4 shows, all the models of reaction have a coefficient of correlation higher than 0.95. Using Avrami-Erofeev A2 model, the activation energy $E_a$ of the isothermal decomposition of the AUC powder was found to be 27.36 kJ mol$^{-1}$ and $\ln A = 1.68$ mm$^{-1}$.

Monshi et al.\textsuperscript{20} have investigated the isothermal decomposition of un-irradiated and pre-\gamma-irradiated dehydrated uranyl acetate at different temperatures between 573 and 593 K. The activation energy values were found to be $E_a = 71.15$ and 26.31 kJ mol$^{-1}$ for the un-irradiated and pre-irradiated sample, respectively. In comparison with our previous study (Korichi et al. 2017),\textsuperscript{1} we find that the value of the activation energy is slightly higher in the case of AUC decomposition under non-isothermal conditions than under isothermal conditions.

**Conclusion**

This study confirms that AUC is decomposed to the tri-uranium octoxide ($U_3O_8$) at $T = 500^\circ$C under air atmosphere. The characterization results of the raw and treated AUC
samples (pore size and pore size distribution, particle size, pore volume, and specific surface area) show the change in the textural properties of U₃O₈ powder obtained from the isothermal decomposition of AUC at $T = 500^\circ$C.

Using model-free (iso-conversional) method, kinetic parameters were estimated at different conversion fractions ($\alpha = 0.1–0.9$) in air atmosphere. Results show that the activation energy ($E_a$) is in the range of 32.15–42.60 kJ mol⁻¹.

Using model-fitting (conventional) method, we noticed the Avrami-Erofeev A2 model that correlates well with our experimental data. We conclude that the Avrami-Erofeev A2 model characterizes and explains the kinetics of AUC isothermal ignition process reaction. The kinetic parameters were estimated at different conversion fractions ($\alpha = 0.1–0.9$). Results show that the activation energy ($E_a$) is in the range of 27.36–32.10 kJ mol⁻¹.

Using the model-fitting method, the nucleation and growth model (Avrami-Erofeev A2) can be successfully applied to the kinetics of AUC isothermal decomposition reaction, and the activation energy is found to be 27.36 kJ mol⁻¹, using the AUC powder with 44-μm mean size fraction.

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References
1. Korichi S, Mernache F, Benaouicha F, et al. J Rad Nucl Chem 2017; 314: 923–934.
2. Slycke1 JT, Mittemeijer EJ and Somers MAJ. Thermo Surf Eng Steels 2015; 3:111.
3. Vyazovkin S, Chrissafis K, Laura Di Lorenzo M, et al. Therm Acta 2014; 590: 1–23.
4. Vyazovkin S, Burnham AK, Criado JM, et al. Therm Acta 2011; 520(1–2):1–19.
5. Remy E, Picart S, Delahaye T, et al. J Nuc Mat 2014; 448: 80–86.
6. Setty DS, Kapoor K and Saibaba N. Prog Nuc En 2017; 101(Pt. A): 100–117.
7. Liu BG, Peng JH, Srinivasakannan C, et al. Ann Nuc En 2015; 85: 879–884.
8. Li Y, Penga J, Liua B, et al. Nuc Eng Design 2011; 241: 1909–1913.
9. Halldahl L and Sorensen T. Therm Acta 1979; 29: 253–259.
10. Halldahl L and Nygren M. Therm Acta 1984; 72: 213–218.
11. Bing-Guo L, Jin-Hui P, Srinivasakannan C, et al. Ann Nuc En 2015; 85: 879–884.
12. Wang YM, Chen QD and Shen XK. Chin Chem Lett 2017; 28: 3–18.
13. Asadi Z and Ranjekesh Shorkaei M. Spec Acta Part A: Mol Biom Spect 2013; 105: 344–351.
14. Savchenkov AV, Peresypkina EV, Pushkin DV, et al. J Mol Str 2014; 1074: 583–588.
15. Khawam A and Flanagan DR. J Phy Chem B 2005; 109: 10073–10080.
16. Naushad A, Manawwer A and Meshary Al-Otaibi AN. Prog React Kin Mech 2015; 40(1): 86–94.
17. Korichi S, Elias A, Mefti A, et al. App Clay Sci 2012; 59–60:76–83.
18. Sreenivasan NL, Srinivasan TG and Vasudeva Rao PR. *Rad Nuc Chem Lett* 1994; 188(6): 463–470.

19. Baldea A, Axente D, Abrudean M, et al. *J Rad Nuc Chem* 1987; 11: 423–428.

20. Monshi MAS, Abd El-Salam NM and Mahfouz RM. *Therm Acta* 1998; 322: 33–37.