Journal of Crystal Growth 441 (2016) 117–123

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

The nucleation kinetics of ammonium metavanadate precipitated by ammonium chloride

Guangchao Du [a,b], Zhaohui Sun [a,b], Yong Xian [a,b], Han Jing [a,b], Haijun Chen [a,b], Danfeng Yin [a,b]

[a] State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization, Panzhihua 617000, China
[b] Pangang Group Research Institute Co., Ltd., Panzhihua 617000, China

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form
2 February 2016
Accepted 12 February 2016
Communicated by Y. Furukawa
Available online 20 February 2016

Keywords:
A1. Activation energy
A1. Induction period
A1. Interfacial tension
A1. Nucleation
B3. Raman spectrum
B1. Vanadates

ABSTRACT

The nucleation kinetics of ammonium metavanadate (NH_4VO_3) was investigated under conditions of the simulated process for precipitation of NH_4VO_3 from the vanadium-containing solution. Induction periods for the nucleation of NH_4VO_3 were experimentally determined as a function of supersaturation at temperatures from 30 to 45 °C. Using the classical nucleation theory, the interfacial tension between NH_4VO_3 and supersaturated solution, the nucleation rate and critical radius of nucleus for the homogeneous nucleation of NH_4VO_3 were estimated. With temperature increasing, the calculated interfacial tension gradually decreased from 29.78 mJ/m^2 at 30 °C to 23.66 mJ/m^2 at 45 °C. The nucleation rate was found to proportionally increase but the critical radius of nucleus exponentially decreased, with increase in supersaturation ratio at a constant temperature. The activation energy for NH_4VO_3 nucleation was obtained from the relationship between temperature and induction period, ranging from 79.17 kJ/mol at $S=25$ to 115.50 kJ/mol at $S=15$. FT-IR and Raman spectrum indicated that the crystals obtained in the precipitation process were NH_4VO_3.

1. Introduction

Ammonium metavanadate (NH_4VO_3) is a crucial intermediate product in the chemical process of vanadium extraction, and it also plays an important role in the preparation of vanadium materials such as catalyst and pigment [1–3]. The crystallization of NH_4VO_3 from aqueous solutions is of both scientific and industrial interest because of its importance in purification of vanadium compounds [4,5]. Industrial production of NH_4VO_3 usually undergoes several processes including the addition of ammonium agent such as ammonium chloride (NH_4Cl) or ammonium sulfate ($(NH_4)_2SO_4$) to vanadium-containing solution, reaction and crystallization at alkalescent condition, washing and filtrating the formed crystals [6]. The formation of large and uniform crystals with less impurity such as silicate and phosphate is desired in achieving a better filtration and application performance of NH_4VO_3 [7]. However, excess ammonium agent, sometimes 2–3 times higher than the stoichiometric amount has to be added to obtain a higher precipitation efficiency and recovery rate of vanadium [8,9], then plenty of NH_4VO_3 crystals form in a short time that causes the increase in ratio of fine crystals and a poor particle size distribution in the precipitation slurry. It leads to the decrease in filtration efficiency of NH_4VO_3 from the precipitation slurry, and the impurities (e.g. phosphate and silicate) in the precipitation solution have more opportunities to enter the products by complexation with vanadium in the crystal lattice and lower the purity of obtained NH_4VO_3 due to more defects of crystals caused by the fast nucleation and crystallization, which also poses a challenge to the purification of vanadium-containing solution [10]. Furthermore, a large amount of waste water containing high concentration of ammonium is produced in the precipitation process which has adverse impact on the environment [11–13]. All the problems mentioned above are strongly related to the process of crystallization, especially the kinetics of nucleation [14–17]. Crystal nucleation is the start of phase transition during which nuclei of the crystalline phase are formed and eventually grow out to macroscopically large crystals, thus is the first and most important step of crystallization [18–21]. Therefore, the kinetics of NH_4VO_3 nucleation in aqueous solutions must be adequately understood in order to provide a better control for crystallization and waste discharge, and obtain crystals with high purity and excellent filtration properties. Meanwhile, like any other generic scientific issues in crystallization the nucleation kinetics of NH_4VO_3 is worthy to be investigated which is important to the basic theories for vanadium industry.

There are a few investigations reported on the nucleation or crystallization of NH_4VO_3 in aqueous solutions. Duan has investigated the crystalline mechanism of NH_4VO_3 mainly including the effects of addition amount of ammonium, temperature and time of precipitation on the morphology of NH_4VO_3 crystals [22]. Gao et al. and coauthors have studied the crystallization kinetics of NH_4VO_3 in the process of vanadium precipitation, mainly focusing on determination

http://dx.doi.org/10.1016/j.jcrysgro.2016.02.016
0022-0248/© 2016 Elsevier B.V. All rights reserved.

of the rate equation and constant for the precipitation of NH_4VO_3 [23]. However, the nucleation kinetics of NH_4VO_3 crystallization has not been understood clearly and experimentally studied, and the parameters for NH_4VO_3 nucleation such as induction period, interfacial tension, nucleation rate and activation energy, etc. also remain unknown. The induction period, t_{ind}, defined as the time elapsed between the creation of supersaturation and the first appearance of a new phase (first detectable changes in solution properties), is an important parameter for nucleation kinetics and is often determined experimentally [24,25]. Interfacial tension between the crystal phase and aqueous solution is a fundamental parameter based on which the nucleation kinetics model can be established, and parameters like nucleation rate defined as the number of formed nuclei per unit time per unit volume can be determined [26]. The activation energy, referring the energy needed for excitation of nucleation, is a crucial index indicating the nucleation kinetics under certain conditions (e.g. supersaturation and temperature, etc.) [27,28]. This paper presents an experimental study on the nucleation kinetics of NH_4VO_3 from solutions containing NH_4Cl and NaCl. The kinetics parameters for NH_4VO_3 nucleation such as induction period, interfacial tension and activation energy were obtained and discussed.

2. Experimental

2.1. Materials

Ammonium metavanadate (NH_4VO_3, mass fraction purity $\geq 99.0\%$) and sodium metavanadate ($NaVO_3$, mass fraction purity $\geq 99.0\%$) were provided by Xilong Chemical Plant, China. Ammonium chloride (NH_4Cl, mass fraction purity $\geq 99\%$), sodium chloride (NaCl, mass fraction purity $\geq 99.5\%$), ammonium bicarbonate (NH_4HCO_3, mass fraction purity $\geq 99\%$) and sodium hydroxide (NaOH, mass fraction purity $\geq 99\%$) were purchased from Kelong Chemical Plant, China. All chemical agents used in the experiments were analytical grade without further purification. The specific conductivity of doubly distilled water in the experiments, measured in a flow cell by a conductivity meter (S230, Mettler Toledo) equipped by an electrode (Inlab 741-ISM, Mettler Toledo) with measurement range of 0.001–500 $\mu S\ cm^{-1}$, was less than 0.1 $\mu S\ cm^{-1}$ at room temperature.

2.2. Reaction and crystallization

NH_4VO_3 can be formed by reaction of $NaVO_3$ with NH_4Cl as follows:

$$NaVO_3 + NH_4Cl \rightarrow NH_4VO_3 + NaCl. \tag{1}$$

The reaction was carried out under simulated conditions of industrial vanadium precipitation in which overdose NH_4Cl is usually added to achieve a higher precipitation rate of vanadium [7,23]. NaCl as a byproduct in the reaction of Eq. (1) should be taken into consideration because it may affect the nucleation of NH_4VO_3 in terms of ionic strength in aqueous solution, referring to the similar phenomenon found in the crystallization of barium sulfate ($BaSO_4$) and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) in NaCl solutions [29–31]. In all experiments, the total mass of the reaction solution was 550 g. The mass fraction of excess NH_4Cl was 2 wt% and mass fraction of NaCl was 3 wt% of the reaction solution. According to Eq. (1), the stoichiometric mass of $NaVO_3$, NH_4Cl and NaCl was separately calculated and denoted as m ($NaVO_3$), m (NH_4Cl) and m (NaCl) respectively at a given temperature and supersaturation ratio, and the additional amount of NH_4Cl and NaCl in the experiments was calculated as m (NH_4Cl)+11.0000 g and 16.5000 g – m (NaCl). Stock solution (1) of total 400 g was prepared by dissolving desired amount of $NaVO_3$ and NaCl (m ($NaVO_3$) and 16.5000 g – m (NaCl)) in doubly distilled water, and the solution pH was adjusted at 8.5 ($\pm$0.1) by NaOH aqueous solution (mass fraction = 30 wt%). During the pH adjustment, NaOH aqueous solution was added dropwise into stock solution (1) mixed by a Teflon-coated stirring bar and a pH meter (PHS-3C, INESA in Shanghai) was used for the pH monitoring. Stock solution (2) of total 150 g containing desired amount of NH_4Cl (m (NH_4Cl)+11.0000 g) was prepared with doubly distilled water. During preparation of the stock solutions, the actual addition amount for each component was the theoretical value divided by the purity. The stock solutions (1) and (2) were then respectively filtered twice through 0.2-μm membrane filters to minimize the amount of insoluble particles, and maintained at desired temperature (30, 35, 40 or 45 °C for the corresponding experiments) before they were mixed. The reaction and crystallization of NH_4VO_3 took place in a jacketed pyrex glass reactor (1000 ml) kept at a constant 30, 35, 40 or 45 °C (within 0.1 °C) by circulating water from a constant-temperature water bath. The solution (2) was added gradually into solution (1) previously placed in the reactor with constant agitation at 300 rpm by a Teflon-coated stirring bar. A condenser was mounted above the reactor in order to avoid evaporation and resultant changes in solute concentrations.

2.3. Determination of induction periods

The induction period (t_{ind}) for NH_4VO_3 nucleation was determined by monitoring the variations in the solution turbidity. Samples of reaction mixture were withdrawn at different time intervals to measure the turbidity during the reaction and crystallization using a turbidimeter (WGZ 2000, INESA in Shanghai) which was calibrated respectively using turbidity standard solution of 2, 20, 200, 500, 1000 and 2000 NTU. Withdrawing a sample and measuring the turbidity took only a few seconds, thus the turbidity was measured at almost the crystallization temperature. The time between achievement of supersaturation by addition of reactants and first obvious change in turbidity was defined as the induction period here. The turbidity was plotted against the crystallization time to obtain the induction period of NH_4VO_3 nucleation. Fig. 1 presents a typical example of obtained plot by this method. It can be seen that the turbidity increases very slowly at the beginning and then suddenly increases. We fitted the data in the regions respectively corresponding the slow and rapid increase of turbidity with crystallization time, and the time corresponding to the intersection point of the two fitted straight lines (red dotted lines in Fig. 1) was determined as the induction period (1164 s in this case). It should be mentioned that the slight increase in turbidity at the beginning of crystallization (see Fig. 1) is perhaps caused by part of unavoidably occurred local nucleation, and we neglect this effect for simplification according to references [14,17].

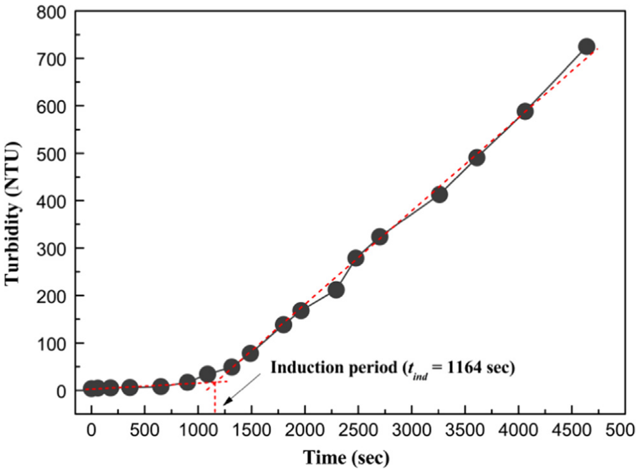

Fig. 1. Relationship between turbidity and time at a supersaturation ratio $S=35$ and a temperature $T=30$.