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Thermal decomposition of ammonium metavanadate in a fluidized bed reactor

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Abstract

Studies on the decomposition of ammonium metavanadate (AMV) in the presence of O_2 were carried out in a fluidized bed reactor. The ammonia gas thus released was passed directly into hydrochloric acid solution of known initial pH and the change in pH of the solution was monitored as a function of time and temperature. The degree of decomposition α was calculated at intermediate stages of the reaction. The overall decomposition pattern was found to fit well into the 'Power-law' kinetic equation. The fluidized bed reactor was found to be effective in achieving a substantial reduction in both the time and temperature required for the complete decomposition of AMV to V_2O_5. The activation energy and rate constant for the overall reaction were determined to be 12.54 ± 0.44 kJ mol^{-1} and 1.4×10^{-3} s^{-1} respectively. The value of the activation energy suggests that the process is surface-area controlled.

Keywords: Activation energy; Ammonium metavanadate; Decomposition; Fluidized bed; Vanadate; XRD

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1. Introduction

Ammonium metavanadate (AMV) is a well-known industrial chemical, widely used as a catalyst for the syntheses of many inorganic and organic compounds [1–4]. It also plays an important role in the preparation and purification of vanadium compounds. In the chemical process of vanadium extraction, the purifica-

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tion of vanadium-containing solutions is generally achieved through a number of successive operations involving the precipitation and dissolution of AMV.

The production of high-purity vanadium pentoxide from red cake ($Na_2H_2V_6O_{17}$) or technical grade V_2O_5 (≈90% pure) essentially involves three steps: (i) dissolution of red cake in soda ash solution, (ii) precipitation of AMV by the addition of an ammoniating reagent such as ammonium chloride (NH_4Cl) or ammonium sulphate (NH_4SO_4), and (iii) calcination of AMV to pure V_2O_5. The chemical reactions involved in the above steps are as follows:

Dissolution of red cake

$$Na_2H_2V_6O_{17}(s) + 2Na_2CO_3(s) = 6NaVO_3(l) + 2CO_2(g) + H_2O(l) \tag{1}$$

Precipitation of AMV

$$NaVO_3(l) + NH_4Cl(l) = NH_4VO_3(s) + NaCl(l) \tag{2}$$

Calcination of AMV

$$2NH_4VO_3(s) = V_2O_5(s) + 2NH_3(g) + H_2O(g) \tag{3}$$

Calcination of AMV is normally carried out in a static bed at temperatures between 450 and 550°C for a period ranging from a couple of hours to twenty-four hours.

Complete decomposition of AMV is essential as the presence of any undecomposed fraction in the final product would interfere adversely in the subsequent chemical processing or its reduction to metal. A survey of the literature has revealed that most of the studies pertaining to the decomposition of either pure AMV or AMV doped with certain metal oxide/hydroxide additives [5,6] have been carried out in a static bed.

In the present investigation, studies on the decomposition of AMV in the presence of O_2 were carried out in a fluidized bed reactor with a view to obtaining an alternate process for the preparation of V_2O_5. Due to the excellent heat and mass transfer characteristics which can be achieved in a fluidized bed reactor, it is expected that the thermal decomposition of AMV under these conditions would reduce both time and temperature.

The data collected in the experimental studies were analysed using standard non-isothermal kinetic equations in order to determine the activation energy for the overall process.

2. Experimental

2.1. Materials

The different chemicals and gases used in the experiment are listed below with a brief description of their functions in this work.

Vanadium pentoxide. Technical grade V_2O_5 (≈90% purity) was used as the starting material for obtaining pure AMV.

Sodium carbonate. Sodium carbonate in water was used for taking solid V_2O_5 into solution.

Ammonium chloride. Ammonium chloride made it possible to precipitate vanadium from aqueous solution in the form of AMV.

Oxygen. Oxygen was used as a fluidizing medium (both for determining the minimum fluidizing velocity and for carrying out the decomposition of AMV) and was drawn from a commercial oxygen cylinder.

Hydrochloric acid solution. Hydrochloric acid solution of known initial pH was kept in a beaker. The evolved ammonia gas was passed through this. The change in pH of the solution was continuously monitored to evaluate the degree of decomposition of AMV.

Ammonium hydroxide. Ammonium hydroxide solution was necessary to maintain the pH in the desired range (8–9) for achieving quantitative precipitation.

2.2. Apparatus

The experimental assembly used in this investigation is depicted in Fig. 1. The fluidized bed reactor consisted of a 50 mm diameter and 1000 mm long transparent silica tube, held vertically, inside which a porous fritted silica distributor was welded above a calming section of 300 mm height.

A vertically placed nichrome resistance furnace was used to heat the fluidized zone of the reactor. The temperature of the bed during decomposition was monitored by a chromel–alumel thermocouple placed at the outer wall of the fluidizing zone as shown in the figure. The difference in temperatures between the outer wall of the silica tube and inside the fluidizing zone was found to be ±2°C.

2.3. Procedure

2.3.1. Preparation of ammonium metavanadate

A solution containing 80 g of soda ash in 500 ml of water was prepared. The solution was heated to 80–90°C and 200 g of technical grade vanadium pentoxide (Table 1) was slowly dissolved into it with continuous stirring. A slow addition of the solute was found to be necessary in order to prevent excessive foaming caused by evolution of CO_2. About 2 g of sodium chlorate ($NaClO_3$) was mixed during dissolution to ensure a pentavalent state for the vanadium. The sodium metavanadate thus formed was treated with NH_4Cl solution (prepared by dissolving 350 g of NH_4Cl in 550 ml of H_2O and heated to 60°C) maintaining the pH at 8.5 by adding ammonium hydroxide solution. The creamy white precipitate thus formed was filtered, washed with a dilute solution (5%) of NH_4Cl and dried at 90°C. The AMV powder thus obtained was analyzed to ascertain its purity (Table 2).

In the second stage of the operation, AMV powder was further dried at 110°C for 24 h in order to make it free-flowing for fluidization. The particle size of the powdered AMV was restricted within the range of 125–250 μm.

Thus in a single-stage dissolution and reprecipitation step, it was possible to obtain reasonably good quality V_2O_5 from technical grade V_2O_5 by keeping the total alkali metal concentration to a significantly low value (Table 2).

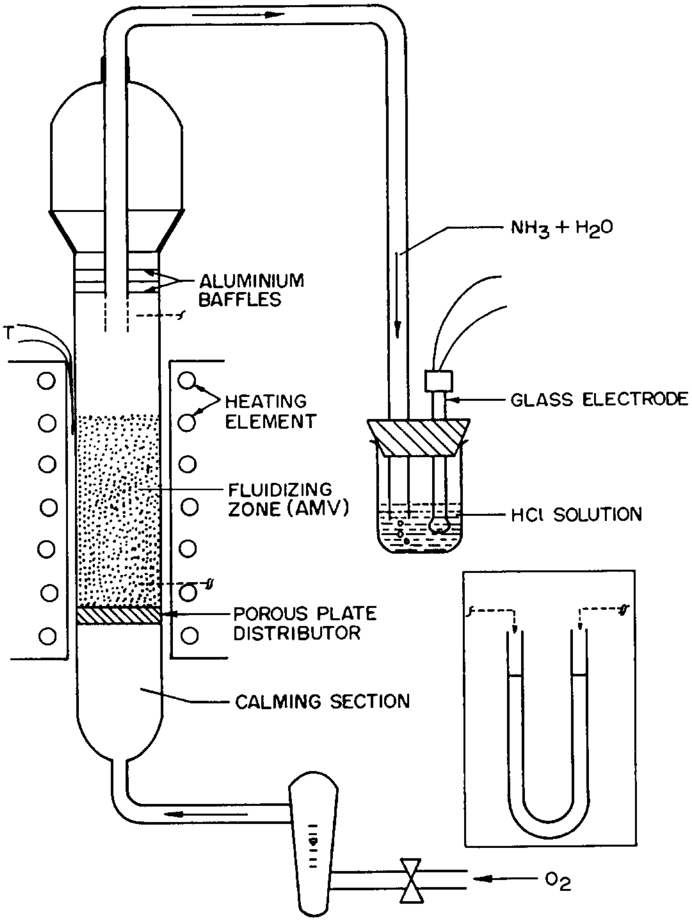

Fig. 1. Experimental set-up for fluidized bed decomposition.

Table 1
Chemical analysis of technical grade vanadium pentoxide V_2O_5

Composition	Amount in wt%	Composition	Amount in wt%
V_2O_5	90.40	Fe	0.05
$Na_2O + K_2O$	9.00	Cu	0.02
SiO_2	0.50	P	0.04

Table 2
Analysis of fully decomposed ammonium metavanadate NH_4VO_3

Composition	Concentration in wt%	Composition	Concentration in wt%
V_2O_5	99.50	P	0.04
Si	0.30	Cu	0.02
Na	0.05	N	0.01
Fe	0.08	C	0.003

2.4. Determination of the minimum fluidizing velocity U_{mf}

The minimum fluidizing velocity U_{mf} is the most important operational parameter that needs to be determined before carrying out any experiment in a fluidized bed reactor.

Therefore, initial experiments were conducted to determine the minimum fluidization velocity U_{mf} at room temperature. About 300 g of AMV was charged into the reactor giving a bed height of 230 mm. O_2 was passed through the rotameter to the calming section of the reactor and further to the fluidizing zone through the silica distributor. A glass manometer tube (filled with ethyl alcohol, C_2H_5OH), one end of which is immersed inside the expanded bed, was used to measure the pressure drop across the bed against flow rate of O_2. Initially the pressure drop started rising with increase in O_2 flow, but attained a constant value with further increase in flow rate and then started falling (Fig. 2). The flow rate at the beginning of the plateau region, called the minimum fluidizing velocity, was found to be 2.2 l min^{-1}. The plateau region extended up to a flow rate of 7.8 l min^{-1} during which AMV remained in the free-flowing state.

An operating gas flow rate of 3.0 l min^{-1} which corresponds to 1.4 times U_{mf} was chosen for the present decomposition studies.

The decomposition of AMV, in principle, can be carried out by using either air or oxygen as fluidizing medium. It was found that the reproducibility of the results was better with oxygen than air. Therefore, decomposition of AMV was carried out by external heating of the reactor up to 300°C under O_2 flow. The ammonia gas

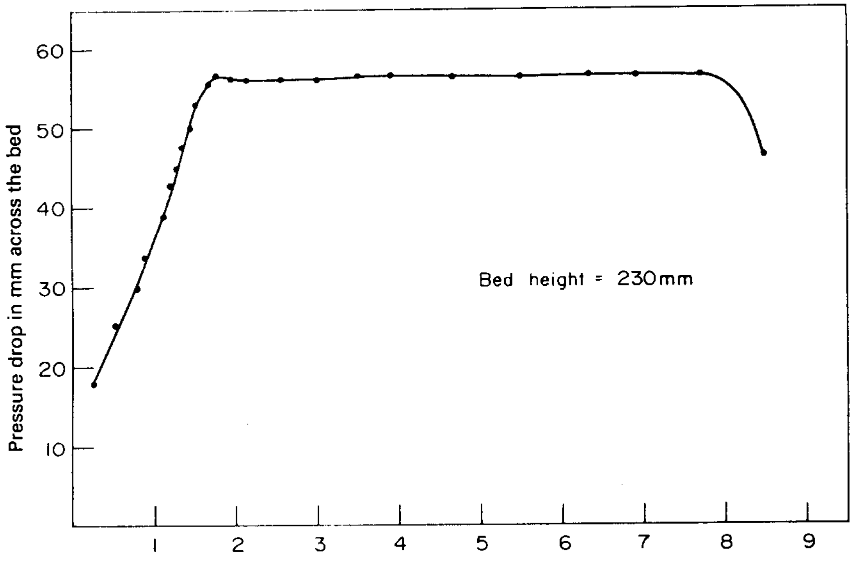

Fig. 2. Determination of minimum fluidization velocity.

thus released was made to pass directly into HCl solution of known initial pH. The change in pH of the solution was monitored continuously (with a glass electrode) throughout the process with respect to time and reactor temperature.

3. Results and discussion

The decomposition of AMV was studied with respect to the following two parameters.

3.1. Temperature

Fig. 3 shows the variation of the extent of decomposition with temperature in the range 180–300°C. The results show a sharp increase in the degree of decomposition in the small temperature range of 180–220°C. The extent of decomposition was 98% by the time the temperature reached 280°C. However, in order to ensure complete decomposition, the temperature was raised to 300°C. The product formed at the end was analyzed by X-ray diffraction (XRD) and chemical analysis. The XRD pattern revealed the presence of only V_2O_5 at 300°C. The results of chemical analyses (Table 2) confirmed the quantitative conversion of AMV to V_2O_5 at 300°C.

3.2. Time

Fig. 4 shows the measured values of pH as a function of time. The graph indicates that initially and up to about 30 min, the pH of the solution remained

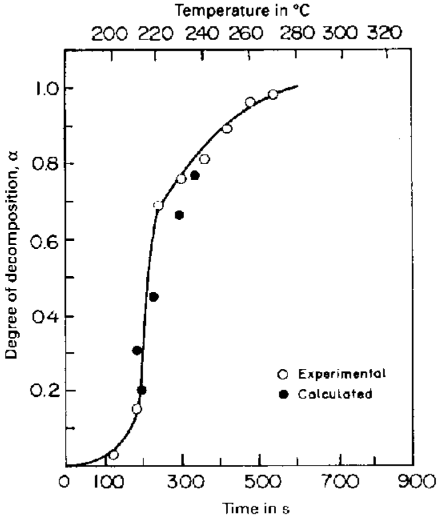

Fig. 3. Degree of decomposition with time and temperature.

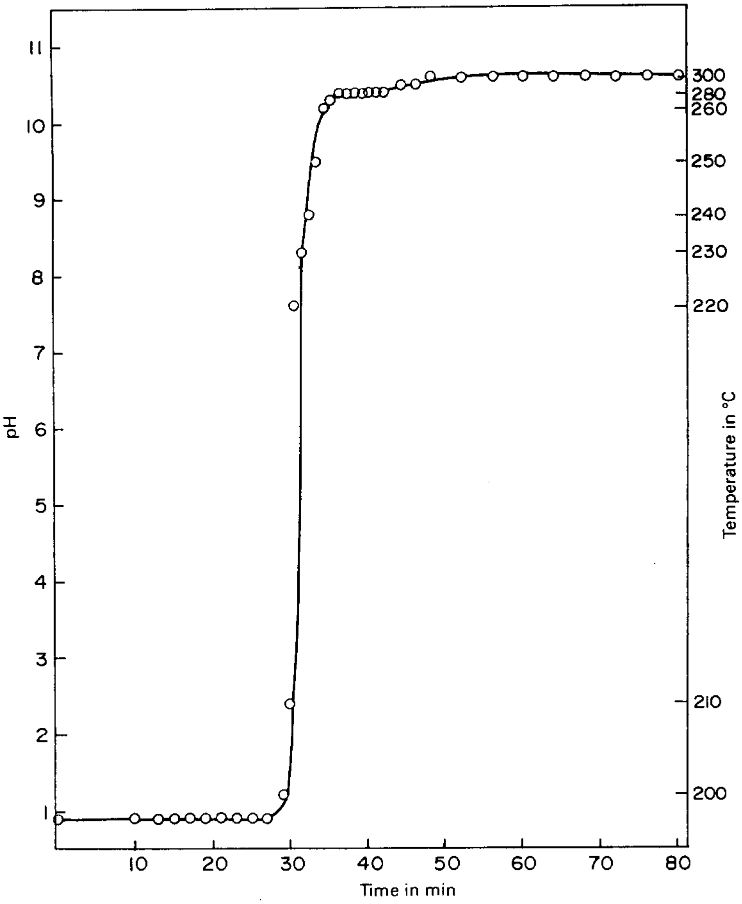

Fig. 4. Measured values of pH with time and temperature.

constant until the temperature reached 180°C, followed by a sharp rise in pH in a small interval of about 200 s, after which a plateau region appeared 280°C. The whole process took about 45 min, indicating a period of nearly 15 min for the complete reaction to take place.

4. Kinetic consideration

The degree of decomposition α (ratio of the volume of solid phase decomposed at time t to the total volume decomposed) was defined as

$$\alpha = (\mathrm{pH_t} - \mathrm{pH_i})/(\mathrm{pH_f} - \mathrm{pH_i}) \quad (4)$$

where pH_i, pH_f and pH_t are the pH values of the solution at $t = 0$, $t = t_f$ (on completion) and at any time t $(0 < t < t_f)$, respectively. The experimental data were found to fit best with the power-law equation [7] which can be represented as

$$d\alpha/dt = k(1/r)\alpha^{1-r} \tag{5}$$

where $r = 1/4$.

The shape of the curve α versus t (Fig. 3) indicates, after a small induction period, a sharp increase in the rate of decomposition of the solid which reflects the growth of the interfacial surface and the autocatalytic acceleration (middle section) of the process concentrated on it. The upper section of the curve exhibits a slowing down of the process due to the deepening of the reaction zone within the lump of the reacting substance and a subsequent reduction in its span [8]. Although in such decomposition processes the shape of the α versus t curve varies greatly with the pressure of the released gas [9], the activation energy, being a physical quantity, does not vary significantly.

The overall activation energy and rate constant for the reaction were determined as 12.54 ± 0.33 kJ mol^{-1} and 1.4×10^{-3} s^{-1} respectively.

Comparing the two possible approaches (both static and dynamic modes of decomposition), it can be said that although the static method undoubtedly gives more information on the reaction mechanism, the dynamic method gives a better indication of the state of the sample at any instant of time with respect to temperature and degree of decomposition [10]. Hence the dynamic method is more suitable for obtaining data on the kinetics of the reaction from a single curve for the whole temperature range.

From a process efficiency point of view, the present investigation offers three distinct advantages over the decomposition process carried out in a static bed reactor. These are (i) avoidance of the formation of an intermediate oxide, V_2O_4, as a decomposition product which is normally found in a static bed if the contents in the reactor are not stirred periodically during the initial stages of the decomposition; (ii) a substantial reduction in the decomposition temperature (300°C as compared to 450°C in a static bed); and (iii) a significant decrease in time (from 5–6 h to even less than an hour for a charge of 300 g).

5. Conclusions

The decomposition of ammonium metavanadate (NH_4VO_3) in a fluidized bed proved to be the most effective method for obtaining V_2O_5 using oxygen as a fluidized medium. The process was accomplished with a substantial reduction in both time and temperature as compared to that in a static bed. The activation energy of the overall process was determined to be 12.54 ± 0.33 kJ mol^{-1}, suggesting a surface-area-controlled reaction. The overall rate constant was found to be 1.4×10^{-3} s^{-1}.

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