TGA/MS STUDIES OF THE THERMAL DECOMPOSITION OF NH_4VO_3

U. VON SACKEN* and J. R. DAHN

Moli Energy Limited, 3958 Myrtle Street, Burnaby, B.C. V5C 4G2 (Canada)

1. Introduction

Many of the reactions used to synthesize intercalation hosts (and other technologically important materials) consume and/or produce gases. Optimizing and scaling up such processes requires a thorough understanding of the reaction mechanism. The method of choice for monitoring such reactions *in situ* is usually thermogravimetric analysis (TGA), but as long as the gases involved cannot be monitored the results may be difficult to interpret. A much better understanding can be obtained by combining TGA with mass spectrometry (MS) of the reaction gases. To illustrate this, we present TGA/MS results for the thermal decomposition of NH_4VO_3 under various atmospheres.

The thermal decomposition of NH_4VO_3 in air is the primary method of producing V_2O_5, but even this well established process is complex and not fully understood [1]. The overall reaction is usually written as

$$2NH_4VO_3 \longrightarrow V_2O_5 + 2NH_3 + H_2O \tag{1}$$

If the decomposition is carried out under a flow of inert gas, oxides ranging in composition from V_2O_5 to V_2O_3 can be produced, presumably because the NH_3 liberated during the initial stages of the decomposition can act as a reducing agent. Products with compositions close to V_6O_{13} are of particular interest as high capacity lithium intercalation hosts. A number of groups [2, 3] have shown that this process can be used to produce non-stoichiometric V_6O_{13} which intercalates 1 Li/V (313 A h kg^{-1}). However, the desired final stoichiometry is difficult to obtain because it depends upon the gas flow, the heating rate, and the reactor design.

2. Experimental

The apparatus used for this work is outlined in Fig. 1. About 50 mg of NH_4VO_3 powder (Fluka 99.5%) were heated in a Dupont TGA under a flow of helium (50 cm^3 min^{-1}) to which reactive gases (O_2 or NH_3) could be
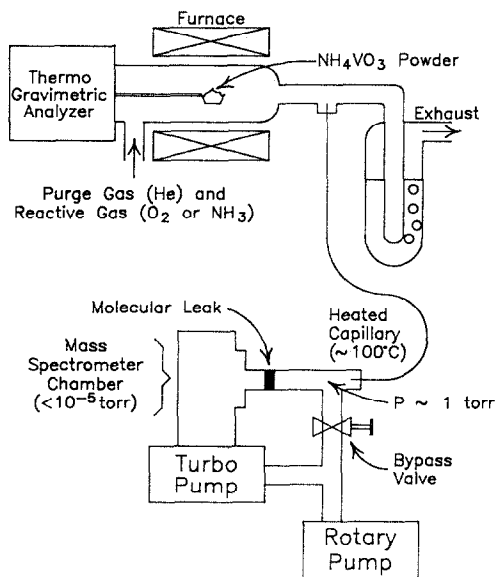
---

*Author to whom correspondence should be addressed.

Fig. 1. Schematic diagram of TGA/MS apparatus.

added (approximately 5 cm^3 min^{-1}). When reactive gases were used they were present in excess throughout the experiment. The sample temperature was ramped at 10 °C min^{-1} while simultaneously monitoring the composition of the effluent gas with a Spectramass quadrupole mass spectrometer. A heated capillary inlet with a bypass was used to give a rapid response time (< 1 s).

3. Results and discussion

Figures 2 - 4 show results for the thermal decomposition of NH_4VO_3 under inert, oxidizing, and reducing atmospheres, respectively. Part (a) of each Figure shows the sample mass (m) and its time derivative (dm/dt). Part (b) of each Figure shows the amount of NH_3, H_2O, and N_2 in the effluent gas. An arbitrary scale is used because the data have not been corrected for the sensitivity of the mass spectrometer to the different gases. The first two peaks in dm/dt (labelled A and B) correspond to the simultaneous evolution of NH_3 and H_2O and are unaffected by the presence of oxygen. In the absence of oxygen, peak C corresponds to the evolution of still more NH_3 and H_2O, but when oxygen is added, most of the ammonia reacts to form H_2O and nitrogen:

$$2NH_3 + 3/2O_2 \longrightarrow 3H_2O + N_2 \tag{2}$$

and peak C shifts to a lower temperature. In the absence of added O_2 (Fig. 2), some N_2 is still detected, so ammonia evidently reduces the solid
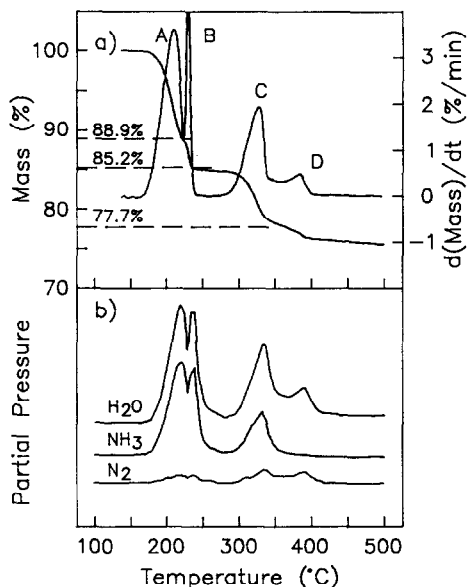
Fig. 2. Thermal decomposition of NH_4VO_3 under an inert gas flow (a) TGA; (b) analysis of the evolved gases.
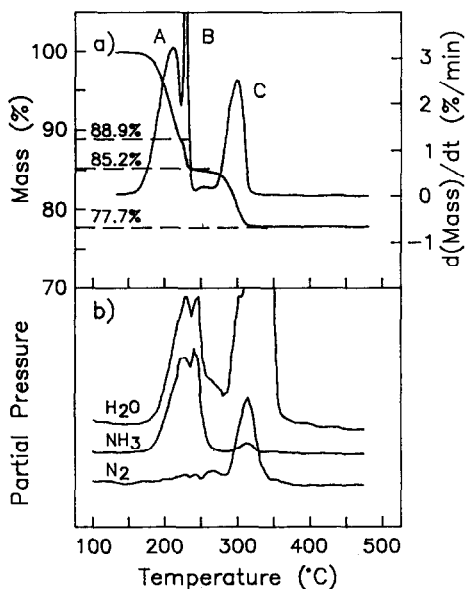

Fig. 3. Thermal decomposition of NH_4VO_3 in the presence of excess oxygen. (a) TGA; (b) analysis of the evolved gases.

residue. The rate of reduction increases with temperature, culminating in a fourth peak (D). If O_2 gas is added it consumes the ammonia gas and peak D disappears. On the other hand, Fig. 4 shows that under excess ammonia,
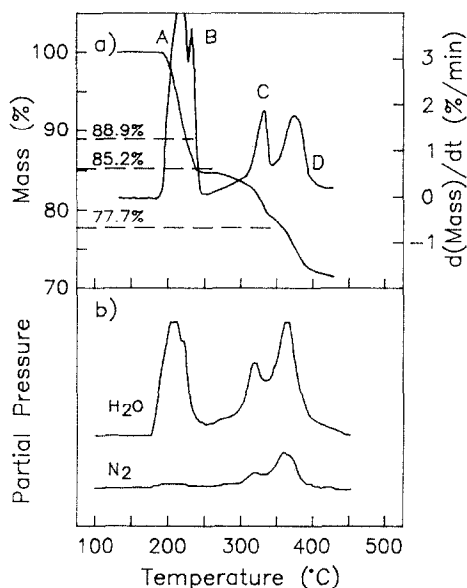
Fig. 4. Thermal decomposition of NH_4VO_3 in the presence of excess ammonia. (a) TGA; (b) analysis of the evolved gases. The partial pressure of NH_3 is not shown because of the high background level due to the added ammonia.

peak D is greatly enhanced. X-ray diffraction patterns show that the final product obtained under excess ammonia is V_2O_3.

Our results indicate that below 250 °C the thermal decomposition of NH_4VO_3 proceeds by the simultaneous release of NH_3 and H_2O in fixed proportion, regardless of whether the atmosphere is oxidizing or inert. This agrees with the generally accepted mechanism [1] shown in Table 1, where NH_4VO_3 is written as $V_2O_5 \cdot (2NH_3 \cdot H_2O)$ to emphasize the proportions of ammonia and water.

Above 250 °C residual ammonia gas plays an increasingly important role as a reducing agent. The rate at which NH_3 reduces the solid is proportional to dm/dt in Figure 4(a), except where peaks A, B, and C are superimposed. From this we see that the reaction rate increases gradually with temperature between 250 and 350 °C, and increases rapidly above 350 °C.

TABLE 1

Decomposition sequence of NH_4VO_3 in an oxidizing atmosphere

Step	Product	% of initial wt.
Starting material	$V_2O_5 \cdot (2NH_3 \cdot H_2O)$	100
A	$V_2O_5 \cdot 1/2(2NH_3 \cdot H_2O)$	88.9
B	$V_2O_5 \cdot 1/3(2NH_3 \cdot H_2O)$	85.2
C	V_2O_5	77.7

The stoichiometry of the final product is determined by the degree to which ammonia reduces the solid residue. Because of this, it is difficult to obtain material with a pre-selected stoichiometry close to V_6O_{13}. The final stoichiometry is highly dependent on sample size, gas flow, heating rate, and reactor design, because these factors determine how much oxygen is removed from the solid during the final step of the reaction. The funamental problem is that V_6O_{13} is an intermediate phase which can only be obtained if the amount of ammonia available at temperatures above 250 °C is carefully limited. Furthermore, unless the reduction proceeds very slowly, the surface is preferentially reduced yielding an inhomogeneous product. The XRD pattern indicates that the final product after TGA under inert gas is a poorly crystallized mixture of V_3O_7, V_6O_{13} and VO_2.

4. Conclusion

We conclude that the stoichiometry of the final product obtained from the thermal decomposition of NH_4VO_3 is governed by the reaction of residual NH_3 gas with the solid residue at temperatures above 250 °C.

Acknowledgements

References

1 S. A. Selim, Ch. A. Philip and R. Sh. Mikhail, *Thermochim. Acta, 36* (1980) 287.
2 D. W. Murphy, P. A. Christian, F. J. DiSalvo, J. N. Carides and J. V. Waszczak, *J. Electrochem. Soc., 128* (1981) 2053.
3 K. M. Abraham, J. L. Goldman and M. D. Dempsey, *J. Electrochem. Soc., 128* (1981) 2493.