GASES RELEASED DURING THE CONVERSION OF $NH_4Zr_2(PO_4)_3$ TO $HZr_2(PO_4)_3$

T. Oi, K. Horio, R. Kikuchi and H. Takahashi

Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyoda, Tokyo 102-8554, Japan

Abstract

Gases released during the conversion of $NH_4Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$ were identified using an apparatus in which gases released from a sample placed in a thermogravimetric analyzer were directly introduced to a gas cell of an IR spectrometer. Such acidic gases as N_2O and NO were detected besides the basic NH_3 gas, and their formation mechanism was discussed.

Keywords: $HZr_2(PO_4)_3$, $NH_4Zr_2(PO_4)_3$, TG analyser connected to IR

Introduction

The rhombohedral $HZr_2(PO_4)_3$, which has originally been studied as an ion conductor [1], shows some unique properties as a cation exchanger. The affinity of $HZr_2(PO_4)_3$ toward alkali metal ions at pH 3.4 is in the decreasing order of $Na^+>Li^+>Cs^+>Rb^+>K^+$ [2], which should be compared with the sequence of $Cs^+>Rb^+>K^+>Na^+>Li^+$ of commercially available organic strongly acidic ion exchangers. Its lithium isotope selectivity is more than ten times larger than those of organic ion exchangers [3].

Experimental

The rhombohedral $HZr_2(PO_4)_3$ is prepared by a heat treatment of $NH_4Zr_2(PO_4)_3$;

$$NH_4Zr_2(PO_4)_3 \rightarrow HZr_2(PO_4)_3 + NH_3, \tag{1}$$

and $NH_4Zr_2(PO_4)_3$ is obtained as precipitate from aqueous solution containing PO_4^{3-}, ZrO^{2+} and oxalic acid with the mole ratio of ZrO^{2+} and $(COOH)_2$ being about 2:3 [4, 5].

Concerning conversion (1), Clearfield *et al.* [1] reported a very interesting observation. When $NH_4Zr_2(PO_4)_3$ was heated at 450°C, the off-gases were acidic while the gases were basic when heated at 700°C. They speculated that acidic gases (nitrogen oxides) were formed by the oxidation of NH_3, with strongly acidic sites created by the removal of NH_3 (i.e. $HZr_2(PO_4)_3$ phase) acting as catalyst.

In order to identify acidic and basic gases released accompanying the conversion of $NH_4Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$ and discuss their formation mechanism, we analyzed the released gases directly by infra-red (IR) measurements during thermogravimetric (TG) measurements of $NH_4Zr_2(PO_4)_3$. The apparatus used consisted of a Perkin Elmer 2000 IR spectrometer and a Perkin Elmer TGA7 TG analyzer, in which gases released from a sample placed in a pan of the TG analyzer were directly introduced to a gas cell of the IR spectrometer by means of a N_2 flow without contacting with the air.

Results and discussion

Figure 1 shows the IR absorbance profiles, as functions of temperature and released gases in TG measurements of $NH_4Zr_2(PO_4)_3$ using a ceramics pan with the heating rate of 50°C min^{-1} (Fig. 1a) or 10°C min^{-1} (Fig. 1b). Contrary to the results of Clearfield et al. [1], only NH_3 (monitored at 966 cm^{-1}) is detected regardless of the heating rate. It is, thus, reasonable to conclude that $HZr_2(PO_4)_3$ is formed by reaction (1) under those conditions.

Similar TG measurements were made using a platinum pan instead of the ceramics one, and the results are depicted in Figs 2a and 2b. When the heating rate is fast at 50°C min^{-1} (Fig. 2a), releases of N_2O (monitored at 2244 cm^{-1} [6]) and NO (monitored at 1917 cm^{-1} [7]) in addition to that of NH_3 are observed between about 300 and
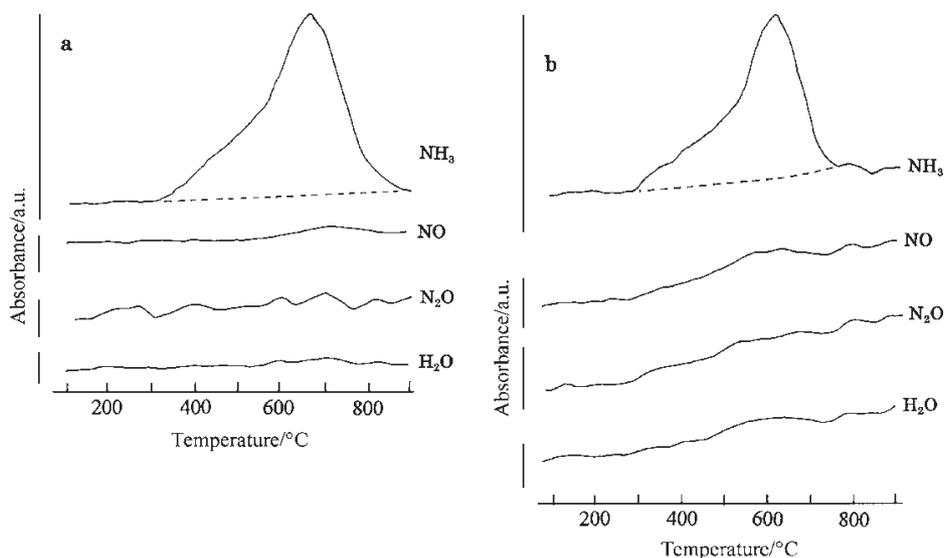

Fig. 1 The IR absorbance profiles of off-gases; a – with the heating rate of 50°C min^{-1} and with a ceramics pan, and b – with the heating rate of 10°C min^{-1} and with a ceramics pan. Note that the scales of the vertical axis are different from figure to figure and from gas to gas

700°C and between about 350 and 800°C, respectively, both accompanied by the release of H$_2$O (monitored at 1597 cm^{-1}). A close examination of Fig. 2a reveals that the NH$_3$ profile has two peaks corresponding to those of N$_2$O and NO. The most plausible reactions of the formations of the two acidic gases, N$_2$O and NO, are:

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \tag{2}$$

and

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{3}$$

With the decrease in heating rate to 10°C min^{-1} and with a platinum pan, the peaks of NO and NH$_3$ disappear and the release of N$_2$O is diminished (Fig. 2b). It is inferred that, when the heating rate is low, the major reaction is;

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{4}$$
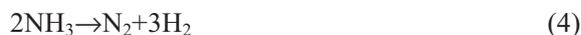
which is undetectable by IR monitoring. Some catalysts must be required for reactions (2)–(4) to occur.

Our above observation shows that platinum used as the material of the pan of the TG analyzer acted as a catalyst for the oxidation of NH$_3$ and contrary to the speculations of Clearfield *et al.* [1], the HZr$_2$(PO$_4$)$_3$ phase did not catalyse the oxidation. It is unknown what kind of materials participated in the heating experiments by Clearfield *et al.* [1]. We claim that HZr$_2$(PO$_4$)$_3$ did not act as catalyst in their experiments, either.
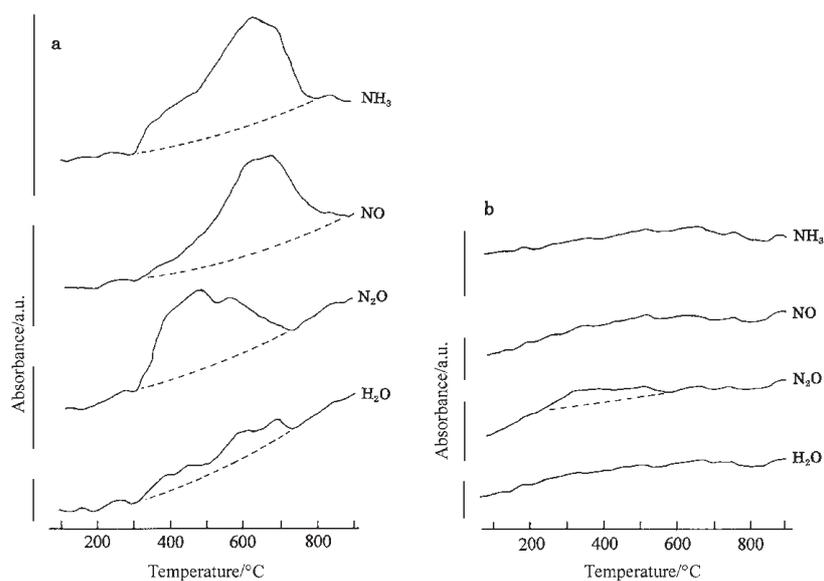

Fig. 2 The IR absorbance profiles of off-gases; a – with the heating rate of 50°C min^{-1} and with a platinum pan, and b – with the heating rate of 10°C min^{-1} and with a platinum pan. Note that the scales of the vertical axis are different from figure to figure and from gas to gas

To summarize, we would like to state that N_2O and NO were identified as acidic off-gases accompanying the conversion of $NH_4Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$ and that the $HZr_2(PO_4)_3$ phase of $NH_4Zr_2(PO_4)_3$ had little catalytic capability for the oxidation of NH_3.

References

1 A. Clearfield, B. D. Roberts and M. A. Subramanian, Mat. Res. Bull., 19 (1984) 219.
2 Y. Nakajima and I. Yoshida, Anal. Sci., 12 (1996) 935.
3 T. Oi, Y. I. Uchiyama, H. Hosoe and K. Itoh, J. Nucl. Sci. Technol., 36 (1999) 1064.
4 Daiichi Kigenso, Chem. Ind., Co., Japan Patent, 6-53566, (1994) 25 (in Japanese).
5 Daiichi Kigenso, Chem. Ind., Co., Japan Patent, 7-115851, (1995) 65 (in Japanese).
6 D. F. Smith, Jr., J. Overend, R. C. Spiker and L. Andrews, Spectrochim. Acta, 28A (1972) 87.
7 R. H. Gillette and E. H. Eyster, Phys. Rev., 56 (1939) 1113.