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MASS SPECTROMETRIC STUDY ON CHEMICAL TRANSPORT REACTION

Michihisa KYOTO, Yoshichika BANDO, and Toshio TAKADA
Institute for Chemical Research, Kyoto University, Uji Kyoto 611

In order to study closed-tube chemical transport reaction process, a mass spectrometer was coupled to a reaction tube. The gases in the ZnO-NH_4Cl transport reaction were analysed with this apparatus. The gas species were Zn, $ZnCl_2$, N_2, H_2O, HCl, and NH_3.

Chemical transport reactions are widely used for the growth of single crystals of inorganic materials. To understand their processes, it is important to know the gaseous species involved in them. Such species have often been assumed from thermochemical considerations, but there have been little experimental evidence for them, although studies with absorption spectrophotometry and vapor pressure measurements have been made in this direction.[1,2)]

We have made an apparatus with a mass spectrometer which enables us to analyse directly the gas species in such reactions, and easily identify each of them with the sensitivity of a few parts per thousand within 1 sec (see Fig.1). The high scanning speed and sensitivity of the spectrometer used (Finnigan 400) made all these possible, even at a highly reduced low pressure of the reaction gas.

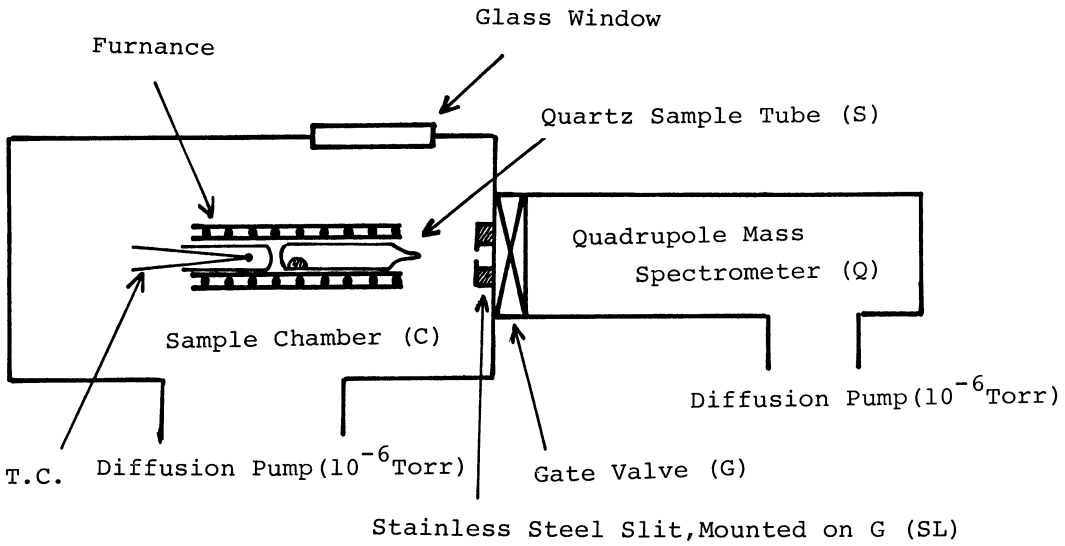

Fig. 1. Schematic diagram of the apparatus

With this apparatus we now studied the chemical transport reaction of ZnO using NH_4Cl as a transport agent. In the literature the following reactions were reported to occur:[3)]

$$ZnO(s) + 2/3\ NH_3(g) = Zn(g) + H_2O(g) + 1/3\ N_2(g) \quad (1)$$

$$ZnO(s) + 2\ HCl(g) = ZnCl_2(g) + H_2O(g) \quad (2)$$

but there are no experimental proofs for the presence of the gaseous species in them.

We proceeded as follows: ZnO sintered at 900°C and NH_4Cl were loaded in S (quartz,3cm long,4mm I.D.), which after evacuated to 10^{-6}Torr, was sealed and placed in C. C was then also evacuated to 10^{-6}Torr, and heated at 640°C for 30-40 minutes. The tip of S was then mechanically broken. The gas produced in S was ejected from the tip and, being collimated with SL and G, entered directly in the ion box of Q. Since the mean free paths of the gas molecules at 10^{-4}Torr are all much longer than the distance between S and the ion box(the distance from the tip of S:10cm), most gas species arrive at the ion box without any change, assuring that the gas species coming into the ion box is the same as those in S.

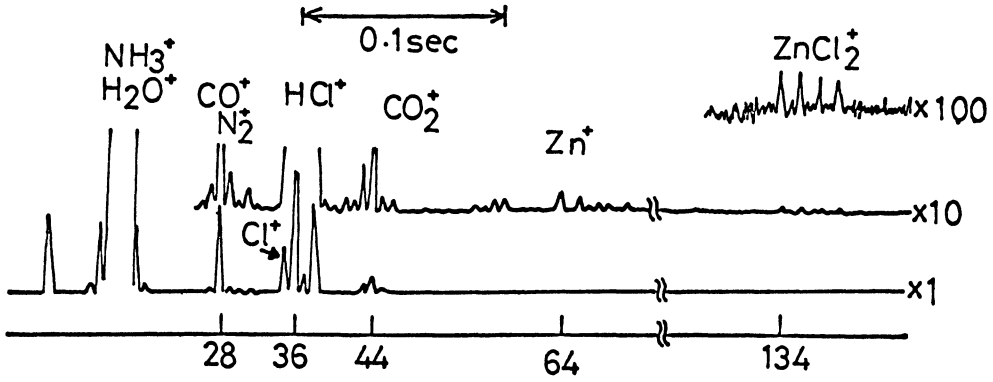

Fig. 2. Typical mass spectrum of gas species in the ZnO-NH_4Cl transport reaction at 640°C (Electron ionization energy: 70 eV).

Fig 2 shows some typical data, with the peaks of Zn^+ at 64,66, and 68 a.m.u. and those of $ZnCl_2^+$ at 134,136,138, and 140 a.m.u.. The peaks of $ZnCl^+$(a fragment from $ZnCl_2$) were observed at 70 eV, but not at 30 eV. CO_2 may be due to the impurity carbon contained in ZnO sample.[4)] It was thus concluded that the gas species in the ZnO-NH_4Cl chemical transport reaction are NH_3,HCl,Zn,$ZnCl_2$,N_2, and H_2O, and the reactions (1) and (2) are reasonable.

We can conclude that this mass spectrometric method is a valuable one for the investigation of the chemical transport reaction.

References

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