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SPECTROPHOTOMETRIC STUDY OF CLOSED-TUBE CHEMICAL TRANSPORT OF VANADIUM OXIDES WITH $TeCl_4$

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The in situ observations of the gaseous species in the closed-tube chemical transport systems, V_2O_3-$TeCl_4$, V_5O_9-$TeCl_4$, VO_2-$TeCl_4$, V_6O_{13}-$TeCl_4$, and V_2O_5-$TeCl_4$ were made by using an UV and VIS spectrophotometer which was improved for the high-temperature measurements. The measurements showed that a great majority of gaseous species in the transport tube is $VOCl_3$ for all the systems, which is in agreement with the earlier result of the mass spectrometry on the VO_2-$TeCl_4$ system.

The vanadium-oxygen system has a series of discrete chemical-shear phases of general formula V_nO_{2n-1}(Magnéli phase) based on a rutile structure.$^{1)}$ Between VO_2 and V_2O_5 there is another series with the formula V_nO_{2n+1}. It was found that many of these phases show the metal-insulator transition which has stimulated the theoretical works on the strong electron-correlation problem.$^{2)}$ The closed-tube chemical transport reactions of these compounds were extensively studied by using $TeCl_4$ as a transport agent.$^{3)}$ Bando et al. proposed the mechanism of the transport reaction of VO_2-$TeCl_4$ system through the direct observation of gaseous species using the mass spectrometry;$^{4)}$ the reactions are $VO_2 + 3/2\ TeCl_4 = VOCl_3 + TeOCl_2 + 1/2\ TeCl_2$ below 700 °C and $VO_2 + 3/2\ TeCl_2 = VOCl_3 + 1/2\ O_2 + 3/4\ Te_2$ above 700 °C. These processes are in agreement with those reported by Oppermann et al. based on the thermodynamic consideration.$^{5)}$

There are only a few reports on the experimental evidence for the gaseous species in the closed-tube chemical transport reaction because of the technical difficulties of the in situ observation of them. Saeki et al. succeeded in the identification of the gaseous species in the halogen transport of V_5S_8 and TiS_2 by in situ observation using the high-temperature spectrophotometer.$^{6)}$ Using the method similar to it, we studied the chemical transport reaction of the system VSe_2-I_2.$^{7)}$ This method has the advantage that it permits the direct observation of gaseous species in the transport tube without extracting them out of the tube. However, the apparatus used by Saeki et al. and us can not be used for the high-temperature measurements above 400 °C due to the thermally emitted radiation.

In the present study we improved the apparatus of the UV and VIS spectroscopy for the use of high-temperature measurements. Using this apparatus, we carried out the in situ observation study of gaseous species in the $TeCl_4$-transport of V_2O_3, V_5O_9, VO_2, V_6O_{13}, and V_2O_5.

The sequence of major components in the spectrophotometers ordinary used is:

Light source --> Monochromator --> Sample --> Detector.

The chief instrumental problem that arises in the high-temperature absorption spectra measurements with this sequence is due to the emission of radiation from the sample, optical cell and furnace. In order to solve this problem, we constructed the instrument with the sequence:

Light source --> Sample --> Monochromator --> Detector.

The schematic diagram of the instrument is illustrated in Fig. 1. This arrangement (modified SS-25 type spectrophotometer: Japan Spectroscopic Co.,Ltd.) made it possible to measure absorption spectra to temperatures of about 1000 °C. The layout of the furnace attached to this instrument is similar to that used in the earlier studies.6-8) The spectra were taken using an evacuated optical quartz cell with the dimension of 10×10×10 mm^3 in which is sealed the mixture of vanadium oxide and $TeCl_4$ with the same molar ratio as in the actual chemical transport.3) The commercial V_2O_3, VO_2, and V_2O_5 were used for the starting materials. V_5O_9 and V_6O_{13} were synthesized from the appropriate mixtures V_2O_3 + VO_2 and VO_2 + V_2O_5, respectively.

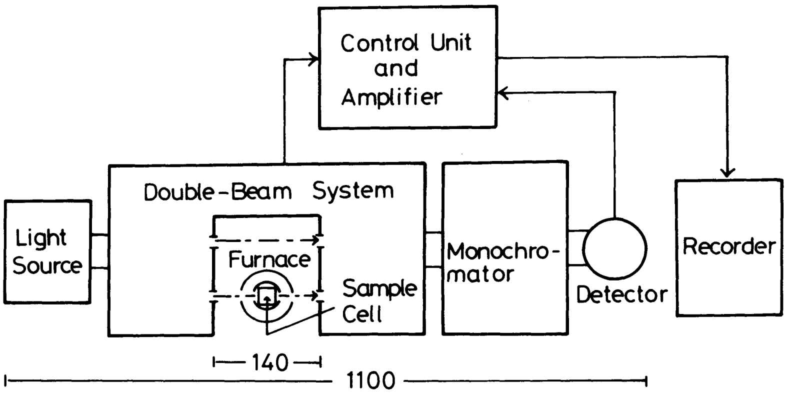

Fig. 1. Schematic diagram of the high-temperature UV and VIS spectrophotometer. The system was constructed by modifying the SS-25 type spectrophotometer of Japan Spectroscopic Co.,Ltd.

As mentioned above, the transport process in the system VO_2-$TeCl_4$ was reported by the earlier authors who claimed that the main gaseous species is $VOCl_3$.4,5) The electronic absorption spectrum of the gaseous $VOCl_3$ was observed in the sealed tube at room temperature by Miller and White.9) But the observation at the higher temperatures has not yet been reported. Using the commercial $VOCl_3$ (Mitsuwa Pure Chemicals Co., 99%), we observed the spectrum of gaseous $VOCl_3$ sealed in an optical quartz cell at temperatures up to 900 °C. Figure 2 shows the observed spectrum of $VOCl_3$ at various temperatures. Two absorption bands were observed, viz. at 243 and 335 nm which are very close to those of Miller and White: 244 and 333 nm. These absorption bands have been assigned to $(1a_2)^2$ --> $(1a_2)(5e)$ and $(1a_2)^2$--> $(1a_2)(6e)$ transitions for 243 and 335 bands, respectively; the state transitions are in both cases $^1A_1$ -> ^1E.10) The spectrum in the present measurements does not change with temperature, which means the gaseous $VOCl_3$ is stable up to 900 °C.

Figure 3 gives the electronic absorption spectrum of VO_2-$TeCl_4$ system at various temperatures. The mixture of VO_2 and $TeCl_4$ was preheated at 300 °C for one

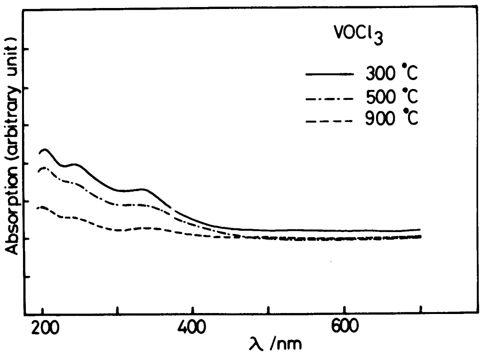

Fig. 2. Electronic absorption spectra of gaseous $VOCl_3$ at high temperatures.

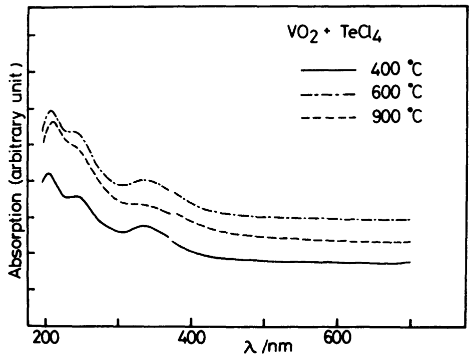

Fig. 3. Electronic absorption spectra of VO_2-$TeCl_4$ system at high temperatures.

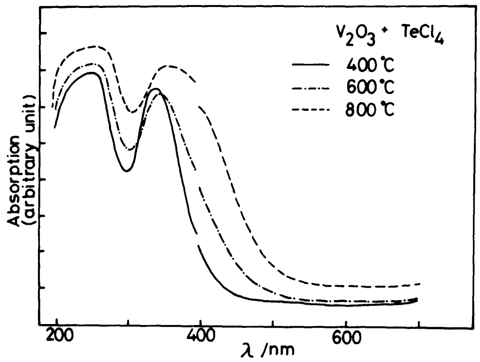

Fig. 4. Electronic absorption spectra of V_2O_3-$TeCl_4$ system at high temperatures.

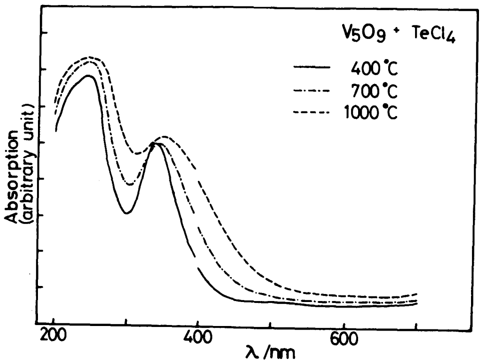

Fig. 5. Electronic absorption spectra of V_5O_9-$TeCl_4$ system at high temperatures.

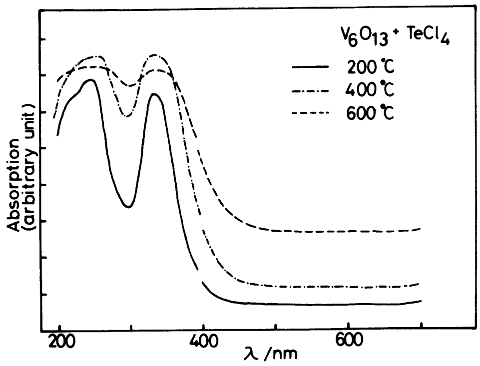

Fig. 6. Electronic absorption spectra of V_6O_{13}-$TeCl_4$ system at high temperatures.

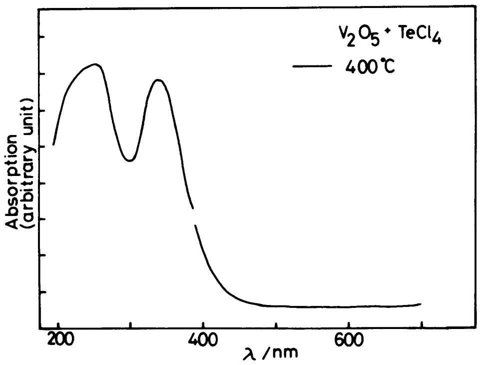

Fig. 7. Electronic absorption spectrum of V_2O_5-$TeCl_4$ system at high temperature.

day. The spectrum in this system is identical with that of $VOCl_3$, and no additional spectrum was recognized in the whole measured temperature-range which means that a great majority of existing gaseous species in this system is $VOCl_3$. This result is in agreement with that of mass spectrometric studies by Bando et al.,$^{4)}$ who reported that the amount of $VOCl_3$ gas is fairly large as compared with that of remaining gaseous species. The amount of each remaining gaseous species is less than 9%. Such a small amount of gaseous species seems to be hardly detectable in the present instrument. In the present study, therefore, we could not find out the temperature-dependence of transport process as early proposed for VO_2-$TeCl_4$ systems.$^{4,5)}$

The spectra of the other systems, V_2O_3-$TeCl_4$, V_5O_9-$TeCl_4$, V_6O_{13}-$TeCl_4$, and V_2O_5-$TeCl_4$ are given in Figs. 4, 5, 6, and 7, respectively. Experimental conditions are same as in the VO_2-$TeCl_4$ system. It is apparent from the figures that the spectrum is fairly identical with that of $VOCl_3$ for these systems. Any other gaseous species except for O_2 gas was not detected. This result is similar to that of VO_2-$TeCl_4$ system. These results suggest that the transport mechanisms are similar to each other in these systems. Thus, it seems that the transport mechanism does not depend on the oxidation states of vanadium atoms in the starting materials varying from V^{+3} to V^{+5} with increasing the oxygen content. However, it is difficult to elucidate the detailed transport processes from the present results, because the remaining gaseous species were not observed.

In conclusion, it was revealed by the in situ observation using the spectrophotometry that the main gaseous species is $VOCl_3$ in the closed-tube chemical transport systems, V_2O_3-$TeCl_4$, V_5O_9-$TeCl_4$, VO_2-$TeCl_4$, V_6O_{13}-$TeCl_4$, and V_2O_5-$TeCl_4$.

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