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ISOTHERMAL REDUCTION OF V_2O_5 BY SO_2 GAS

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When V_2O_5 is reduced isothermally by SO_2 gas (200 cc/min), the weight loss shows the stepwise curve. Each step corresponds to the intermediate phase expressed by general formula V_NO_{2N+1} (N=3,4,5, ... and∞). The quenched specimens at each step analyzed by an X-ray diffraction, however, have revealed to be coexistence of two phases, except for the case of N=4,6 and ∞ (V_2O_4).

The phase equilibrium studies on the V_2O_3-V_2O_4 system have been extensively done and confirmed the existence of many phases (N=3 to 9) in general formula V_NO_{2N-1}.1),2),3) On the other hand, in the V_2O_4-V_2O_5 system, it has been confirmed at present that V_3O_7, V_4O_9 and V_6O_{13} are existing as one phase. In 1957, Wasdley4) suggested that there must be existed many phases expressed by general formula $V_{2w}O_{5w-2}$ (w:integer). Afterwards, Tudo et al.5) and Toda et al.6) prepared V_3O_7 phase (w=6) by the solid state reaction, and Taniguchi et al.7),8),9) for the first time confirmed V_4O_9 (w=4) by the reduction of V_2O_5 by SO_2 gas. Reduction process studies of V_2O_5 by various reducing gases were made by many workers. The preparation process of V_2O_5, V_3O_7, V_6O_{13} and V_2O_4 is summarized schematically in Figure 1.

This letter reports the isothermal reduction of V_2O_5 by SO_2 gas of constant flow rate of 200 cc/min. As the results, the fifteen phases, which correspond to N=2,3,4,5,6,7,8,10,12,13,18,22,23,36,∞ in general formula V_NO_{2N+1}, have been confirmed to be existed as one phase at 430°C.

Starting material V_2O_5 was obtained by decomposition of NH_4VO_3 (99.0 % up) at 500°C in air for a week. Weight loss during reduction by SO_2 gas (200 cc/min) was measured by a spring balance made of quartz, whose sensitivity is more than 0.13 % (TG method). About 150 mg V_2O_5 was placed on a quartz plate (5 mm diameter).

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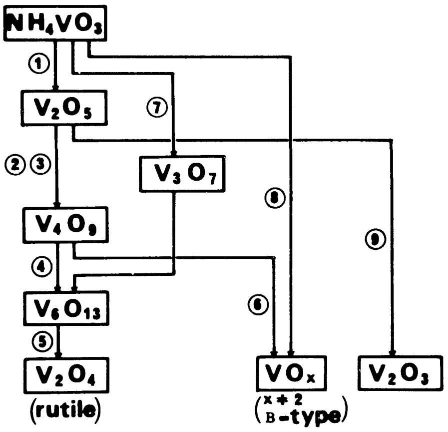

① in air at 500°C

② SO_2 gas (200 cc/min) at 410°C

③ C_4H_6(Butadiene) gas 20% + N_2 gas 80% at 310°C

④ SO_2 gas (200 cc/min) at 470°C

⑤ SO_2 gas (200 cc/min) at 500°C

⑥ C_4H_6(Butadiene) gas 30% + N_2 gas 70% at 370°C

⑦ decomposition in vacuum at 500°C

⑧ H_2 gas at 300°C

⑨ H_2 gas at 800°C

Fig. 1. Reduction Process of V_2O_5 by Various Reducing Conditions.

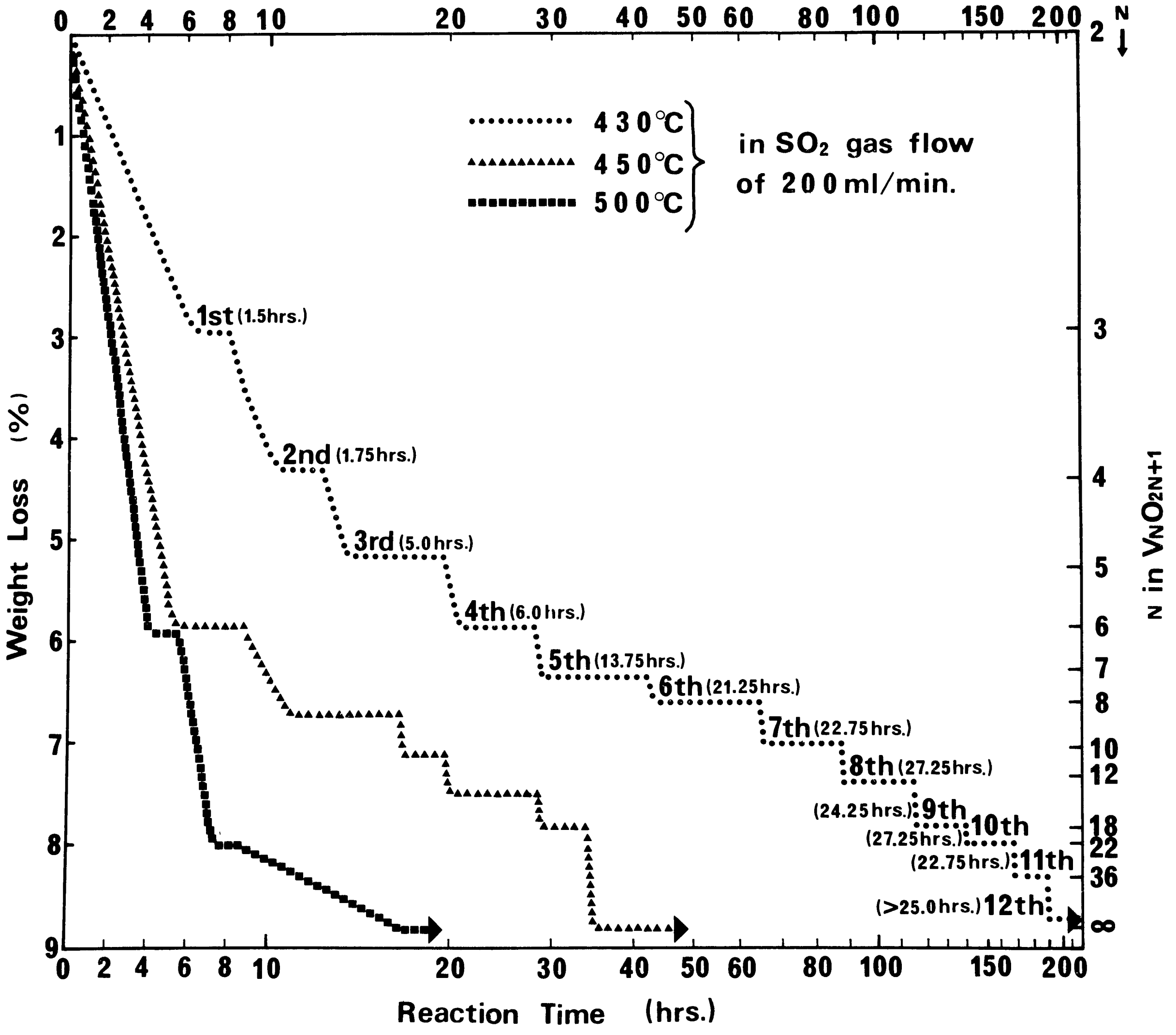

Fig. 2. Isothermal Reduction of V_2O_5 by SO_2 Gas at 430, 450 and 500°C.

SO_2 gas was dried with P_2O_5 and deoxygenated with Cu nets at about 800°C. The temperature of isothermal reduction was varied from 350 to 600°C, which was controlled by a usual on-off temperature controller within ± 2°C. About 30 runs have been performed in different reducing conditions.

Typical examples of the weight loss versus reducing time are shown in Figure 2. This figure shows the stepwise reduction process. The main results obtained are as follows:

1) The lower the temperature, the longer the time of the constant weight (step) keeps and also the more the number of step increases.

11) At constant temperature, the larger the number N in V_NO_{2N+1}, the longer the time of the each step keeps.

111) Each step corresponds to N in general formula V_NO_{2N+1}. We found out the fifteen steps at least, which correspond to N=2,3,4,5,6,7,8,10,12,13,18,22,23,36,∞.

The notable fact is that in order to get many steps and also longer time of constant weight at each step, it is desirable to pack the starting material (V_2O_5) as loose as possible.

Then we tried to get single phase samples corresponding to each N by quenching from reacting temperature to room temperature. Quenched samples were identified by an X-ray powder diffraction (Cu $K_{\alpha 1}$). Some of the examples are shown in Figure 3. As seen in the figure, it was confirmed that only three phases (V_4O_9, V_6O_{13}, and V_2O_4) are able to be quenched as single phase. X-ray powder diffraction patterns of V_2O_5, V_6O_{13} and V_2O_4 are in good agreement with the ASTM card, and that of V_4O_9 is also in excellent agreement with the data of Taniguchi et al.[7),8)] and Theobald et al.[10),11)] For example, in the case of the isothermal reduction at

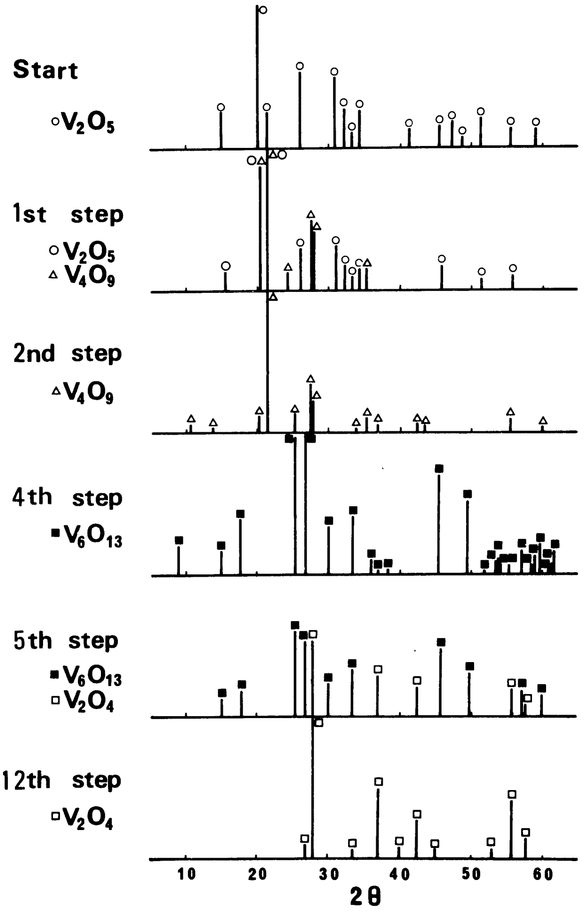

Fig. 3. X-ray Identification of Quenched Samples (Cu $K_{\alpha 1}$)

430°C (See Figure 3), quenched samples of the 2nd, 4th and 12th steps show V_4O_9, V_6O_{13} and V_2O_4 phases respectively. Samples corresponding to the other steps (in this case, the 1st, 3rd and 5th to 11th), however, show two phase mixtures. These peculiar results can be interpreted by following two ways. One possibility is that with the exception of the steps corresponding to V_4O_9, V_6O_{13} and V_2O_4, the samples corresponding to the steps N=3,5,7,8,10,12,13,18,22,23,36 really are two phase mixtures in situ. It is, however, not naively acceptable that on the step the ratio of the quantity of the two phases is constant for a long time and also average composition happens to correspond to N in general formula V_NO_{2N+1}. The another possiblility is that in situ the samples corresponding to each N is really V_NO_{2N+1}, but they can not be quenched to room temperature except for V_4O_9, V_6O_{13} and V_2O_4. The latter possibility is persuasive from the consideration of the crystal structure of V_NO_{2N+1} described below.

Present authors suggested12),13) that crystal structure of V_NO_{2N+1} can be described by the double shear structure, analogous to Magneli phases V_NO_{2N-1}. For the case of V_NO_{2N+1}, the mother structure is ReO_3 type one. The shear structure is constructed as follows; in the first step every n-th plane (200), of oxygens only, perpendicular to a-axis of ReO_3 is regularly eliminated and the structure closed up by shear vector $1/2[101]_{ReO_3}$, and then in the second step every m-th plane (020), of oxygens only, perpendicular to b-axis is regularly eliminated and the structure again closed up by shear vector $1/2[110]_{ReO_3}$. As the results, the new compound with general formula $Me_{nm}O_{2nm-n-m}$ is produced. It is to be noted that if we put n=2, general formula is $Me_{2m}O_{5m-2}$, which is the same formula as the one suggested by Wadsley. It is also easily verified that if N=nm/nm-n-m were satisfied, $Me_{nm}O_{3nm-n-m}$ could be changed to Me_NO_{2N+1}. Table 1 shows the N in V_NO_{2N+1}, the pair (n,m) in $Me_{nm}O_{3nm-n-m}$, the w in $V_{2w}O_{5w-2}$ (Wadsley's notation) and corresponding composition (Metal to oxygen ratio). In these compounds, the crystal structure of $V_2O_5$14), $V_4O_9$11),13), V_6O_{13}15) and $V_2O_4$16) determined by single crystal X-ray and electron diffraction revealed that these compounds can be expressed by the double shear structure (2,∞), (2,4), (2,3) and (2,2) respectively, as shown in Table 1. The crystal structure of V_4O_9 determined by Wilhelmi et al.17) is different from that of ours. The crystal used in their study shows the different X-ray powder patterns from those of Taniguchi et al.'s7),8), Theobald et al.'s10),11) and also ours. This difference may be due to the sample preparation. Wilhelmi et al. got the single crystal by the decomposition of V_3O_7 in super critical water at 600°C

Table 1. Possible Shear Structure of Vanadium Oxides in the V_2O_5-V_2O_4 System[13)]

N in V_NO_{2N+1}	w in $V_{2w}O_{5w-2}$	(n,m) in $V_{nm}O_{3nm-n-m}$	Composition
∞	2	(2,2),(∞,1)	V_2O_4 ($VO_{2.00}$)
6	3	(2,3),(3,2)	V_6O_{13} ($VO_{2.16}$)
5	----	-----------	V_5O_{11} ($VO_{2.20}$)
4	4	(2,4),(4,2)	V_4O_9 ($VO_{2.25}$)
----	5	(2,5),(5,2)	$V_{10}O_{23}$ ($VO_{2.30}$)
3	6	(2,6),(3,3),(6,2)	V_3O_7 ($VO_{2.33}$)
2	∞	(2,∞),(3,6),(4,4),(6,3)	V_2O_5 ($VO_{2.50}$)

and 2 Kb in a sealed gold tube. The crystal structure of V_3O_7 was also determined by Andersson et al.[18),19)] However the structure can not be interpreted as the double shear structure. There remains the possibility that the V_3O_7 produced by reduction by SO_2 gas has the double shear structure (See Table 1).

Now let us discuss on the reduction mechanism of V_2O_5 by SO_2 gas, correlated with the shear structure. As shown in Figure 3, the reduction process shows the repetition of a step (constant weight within the experimental error) and rapid reduction. It has been generally accepted that in the case of the shear structure, a variety of defects, which is due to the anion deficiency, appears in the slightly reduced region and then these anion vacancy clusters into discs (embryo of the shear plane), bounded by dislocation. Steps appeared in the isothermal reduction may correspond to this process. It is necessary for the formation of the embryo of the shear plane to take a lot of time, because there must be existed the competition between annihilation and formation of the embryo. The elastic strain in the vicinity of discs promotes their capacity to act as sinks for further anion vacancies transported by diffusion. Once the embryo of the shear plane has been formed, an anion diffusion becomes very easy and the samples grow into the shear structure very rapidly. This process corresponds to rapid weight loss (rapid reduction). Thus we could estimate the reduction mechanism of V_2O_5 by SO_2 gas, correlated with the shear structure.

In conclusion, we want to point out experiments to be examined in future.

1) It is necessary to take an X-ray diffraction in situ at each step.

11) It is obvious that the above mentioned shear structure model can not apply for the case of N>6. Accordingly the new shear structure model must be put forward by the crystal structure determination of the samples with N>6.

111) The possibility of the existence of new phases with very near V_2O_5 composition, in relation to Tilley et al.'s observation[20), which composition may be corresponding to w>6 in Wasdley's notation or, for example, (3,4),(3,5)... in general formula $V_{nm}O_{3nm-n-m}$.

1V) Sata et al.[21),22) reported the new compounds B and C, which have the composition V_2O_4 and V_6O_{13} respectively (See also reference 23). The crystal structure determination of these compounds is very interesting, in relation to another possibility of the shear structure (See Table 1).

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