Rapid Diffusion of Oxygen Ions in Indium Oxide during Reduction-oxidation

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Synopsis. Rapid diffusion of oxygen ions in indium oxide particles has been suggested by measuring the distribution of ^{18}O ions after oxidation of reduced-indium oxide by $^{18}O_2$ (gas). This result explains the observation that the reduced-indium oxide is one of the most efficient compounds among the reduced metal oxides for reduction of H_2O, CO_2, or NO.

In the previous works we have demonstrated that In_2O_3 is one of the most effective metal oxides to the two step hydrogen production from water which applies reduction (Step 1) and oxidation (Step 2) cycles of the oxide.[1,2] If the Step 1 is operated by using hydrogen for simplicity, the Steps 1 and 2 can be expressed by the following forward and reverse reactions, respectively:[1,3]

$$In_2O_3 + 3H_2 \rightleftharpoons 2In + 3H_2O. \quad (1)$$

When CO_2, NO, or O_2 instead of H_2O was used in Step 2, the following reactions proceeded smoothly at 673 K:[3]

$$2In + 3CO_2 \longrightarrow In_2O_3 + 3CO \quad (2)$$

$$2In + 3NO \longrightarrow In_2O_3 + 3/2\,N_2 \quad (3)$$

$$2In + 3/2O_2 \longrightarrow In_2O_3. \quad (4)$$

In the previous studies we have proposed a mechanism of reduction of In_2O_3 and that of reoxidation of the reduced oxide which assume a rapid diffusion of oxygen ions from the reaction interface at the surface of indium oxide particles into the bulk or vice versa, respectively (homogeneous model).[4] This model inevitably requires an apparent homogeneous distribution of the oxygen ions and indium metals throughout a oxide particle. With regard to this requirement, we intend to describe in this note an experimental proof that the oxygen ions in indium oxide particles distribute homogeneously during their redox cycles.

Experimental

The In_2O_3 used was a reagent-grade powder (purity>99.9 %) obtained from Wako Pure Chemical Co. The BET surface area of the oxide was 13.9 $m^2\,g^{-1}$. The apparatus employed was a conventional mercury-free, greese-free, static gas-circulation system of *ca.* 320 cm^3 volume. The water vapor evolved during the reduction of In_2O_3 by hydrogen was always condensed in a trap which had been placed in the gas-circulation line and cooled at 77 K. Contents of oxygen isotopes in oxygen or water were determined by mass-spectroscopic analysis.

Results and Discussion

After the reduction of In_2O_3 by hydrogen to the degree of reduction of 19.7%, which was estimated from the quantity of oxygen removed from the oxide, the reoxidation by $^{18}O_2$ (98.5% ^{18}O content) was carried out at 673 K. The oxygen ions of the sample thus oxidized by $^{18}O_2$ were stripped by reduction with hydrogen at 623—673 K. The contents of $H_2{}^{18}O$ in the produced water at certain range of reduction levels were measured by mass spectrometer. The change in contents of ^{18}O ions thus determined is demonstrated in Fig. 1 as a function of the degree of reduction of In_2O_3 (solid lines). The hight of bars in the figure indicates the average percentage of ^{18}O ions observed between the each two levels of reduction of the sample oxide.

Let us consider first the distribution of ^{18}O ions in a indium oxide particle. If the reduction of In_2O_3 proceeds from the surface of In_2O_3 particle into the bulk, leaving indium metal layer covering the particle (Fig. 2, model A), we expect the distribution of ^{18}O ions after reoxidation by $^{18}O_2$ as indicated by the chain line (—·—) in Fig. 1. On the other hand, if the oxide ions diffuse rapidly into or from the bulk, resulting in seemingly homogeneous distribution of ^{18}O ions (Fig. 2, model B), the distribution of ^{18}O ions in a particle should be the one indicated by the broken line (----). The experimental results (bars) suggest that the distribution of ^{18}O ions is roughly homogeneous, supporting the propriety of the latter model.

The formation of In_2O by the reduction of In_2O_3 was assumed by several workers.[5–7] However, there are no evidence suggesting the existence of crystalline In_2O.[8–10] Our X-ray spectroscopic studies of the partially reduced In_2O_3 could establish only the existence of In_2O_3 and indium metal. Brewer[8] concluded in

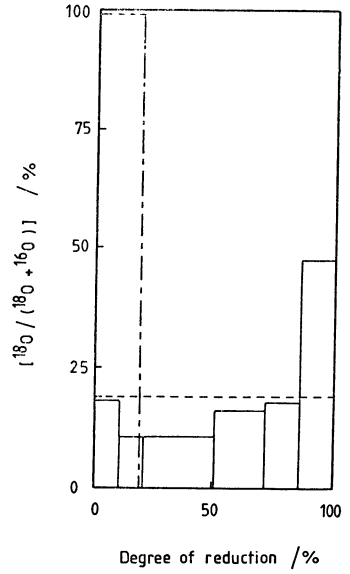

Fig. 1. ^{18}O ions distribution in a particle of the reoxidized indium oxide by $^{18}O_2$(gas). (——); Experimental observation, (—·—); idealized distribution according to the model A, (----); idealized distribution according to the model B or C,

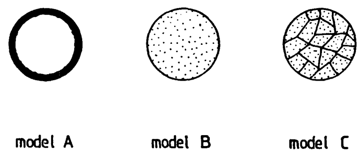

Fig. 2. Schematic model of the distribution of indium metal in the bulk of a particle (sectional views of a particle). Black part or spots are indium metal layer or nuclei. The lines in model C are grain boundaries.

his review that the supporsedly crystalline In_2O is a stoichiometric mixture of indium and In_2O_3 or is a metastable homogeneous phase. Wit *et al.*[10] commented that an indium(I) oxide like In_2O exists only as a parasitic phase, in combination with the contacting indium metal and In_2O_3, and is highly nonstoichiometric. We consider that the model B in Fig. 2 corresponds to the homogeneous mixture of indium metal and In_2O_3 as described above.

The mean dimension of the In_2O_3 crystallites estimated from the half width of X-ray diffraction peaks using the Scherrer's equation[11] was 23 nm. The SEM picture of the sample indicated that the sizes of the particles are in the range of 100—1000 nm. Therefore, the netwarks of the grain boundaries can be assumed to spread over in a particle. The rapid transport of oxygen ions in a particle may be enabled by the short circuit diffusion through these grain boundaries (model C in Fig. 2).

The exchange of $^{18}O_2$ in gas phase with ^{16}O ions of fresh In_2O_3 occurred at temperatures higher than 673 K. The sample of In_2O_3, whose oxygen ions had been exchanged by $^{18}O_2$ at 773 K to the extent of 7.3 atomic percentage of the total oxygen ions of the oxide, was reduced by hydrogen at 623 K stepwise to the degree of reduction of 62% and at 673 K to 90%. The analysis of the produced water indicated the distribution of ^{18}O in the oxide as demonstrated in Fig. 3. The broken line indicates the ideal homogeneous distribution of ^{18}O ions in a In_2O_3 particle or grain. The observed distribution demonstrated by the bar graph in Fig. 3 suggests that the ^{18}O ions have penetrated deep into a In_2O_3 particle or crystal grain, supporting the easy diffusion of oxygen ions from the surface or grain boundaries into the bulk. The high content of ^{18}O at the lowest range of reduction level (0—10%) may be ascribed either to adsorbed oxygen atoms on the surface or to the oxygen atoms at grain boundaries which were equilibrated with $^{18}O_2$ in gas phase during the exchange pretreatment. The rather high concentration of ^{18}O ions at the highest reduction levels indicated both in Figs. 1 and 3 cannot be explained at the moment. They might be the one trapped in dislocations or defects of crystals, resulting in their total stabilization.

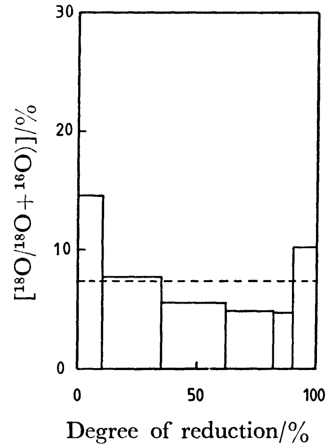

Fig. 3. ^{18}O ions distribution in a particle of In_2O_3 which had been exchanged by $^{18}O_2$(gas). (——); Experimental observation, (----); idealized distribution according to the model B or C.

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