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DEHYDROGENATION OF HYDROGEN MOLYBDENUM BRONZE, $H_{0.3}MoO_3$

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Hydrogen molybdenum bronze, $H_{0.3}MoO_3$, is decomposed through two processes on vacuum heating with evolution of H_2O. One is the low-temperature process without structural change. The other is the high-temperature process with structural change from the bronze to MoO_3* which is a non-stoichiometric MoO_3 structure.

The existence of a series of hydrogen molybdenum bronzes was established by Glemser et al.[1)] Birtill and Dickens[2)] studied phase relationships in the system $H_xMoO_3(0 < x \leqq 2.0)$ and characterized four kinds of phases as (i) blue orthorombic($0.23 < x < 0.4$), (ii) blue monoclinic($0.85 < x < 1.04$), (iii) red monoclinic($1.55 < x < 1.72$), and (iv) green monoclinic($x=2$). In this paper, these phases are denoted as TypeI, Type II, Type III, and Type IV, respectively.

The hydrogen molybdenum bronzes are derived from MoO_3 by insertion of atomic hydrogen. These atoms were expected to be effective for catalytic reaction. Sermon and Bond[3)] and Marcq et al.[4)] have studied the catalytic reaction for pent-1-ene and ethylene hydrogenation on $H_{1.6}MoO_3$(Type III) obtained from Pt-supported MoO_3 by hydrogen spillover. It may be considered that the atomic hydrogens in Type I and Type II are also effective for catalytic reactions. Structural and compositional changes of these Types under vacuum heating have been reported.[5)] However, there is no study on the kinetics of dehydrogenation reaction. This paper deals with the isothermal dehydrogenation of Type I and hydrogen behaviors estimated by proton NMR.

Hydrogen molybdenum bronze of Type I was prepared by Glemser's method[1)] and the X-ray diffraction pattern was consistent with that reported by Birtill and Dickens.[2)] The composition of the samples obtained was determined to be $H_{0.3}MoO_3$ by thermogravimetry and by Choain and Marion's method.[6)] The experimental details have been described elsewhere.[5)]

The samples were heated isothermally at various temperatures(110-446°C) after pretreatment for 1 h at room temperature under a vacuum of 10^{-4} Torr. The change in weight was measured by a Cahn electromicrobalance. The gas eliminated from the samples was analyzed by a quadrupole gas analyzer(NAG-531) and it was confirmed to be only H_2O at all reaction temperatures. Figure 1 shows the fraction reacted(α)-time plot for isothermal dehydrogenation of Type I. These curves obeyed Avrami-Erofe'ev equation.7) This suggests that the reaction proceeds through nucleation process.

$$-\ln(1-\alpha) = kt^n \quad \text{(n is constant)}$$

The n and rate constant k can be determined from the plot of $\ln(-\ln(1-\alpha))$ against ln t. Figure 2 shows that n varies from 0.87 to 2.31 with the rise in heating temperature. This suggests that dehydrogenation process is complicated. The equation, when n=2, means that nucleation is rapid and growth is two dimentional.7,8) An activation energy was determined from the isothermal data by applying the Arrhenius equation, as shown in Fig. 3. A crease appeared at about 330°C. The activation energy in the range above 330°C is 37.0 $\mathrm{KJmol^{-1}}$ and in the range below 330°C, 12.2 $\mathrm{KJmol^{-1}}$, suggesting that there exists different dehydrogenation processes between low- and high- temperature ranges.

In addition to the isothermal results, proton NMR9) was observed in an untreated sample and a sample treated at 350°C under a vacuum of 10^{-4} Torr. Free induction decay(FID)

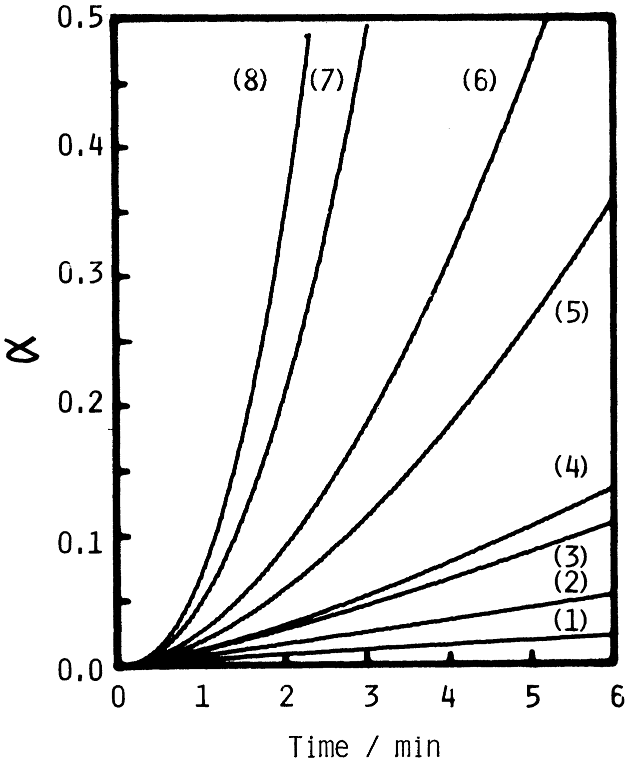

Fig. 1. Isothermal α-time plot of Type I. (1); 101°C, (2);152°C, (3);194°C, (4);238°C, (5); 297°C, (6);349°C, (7);398°C, and (8);446°C.

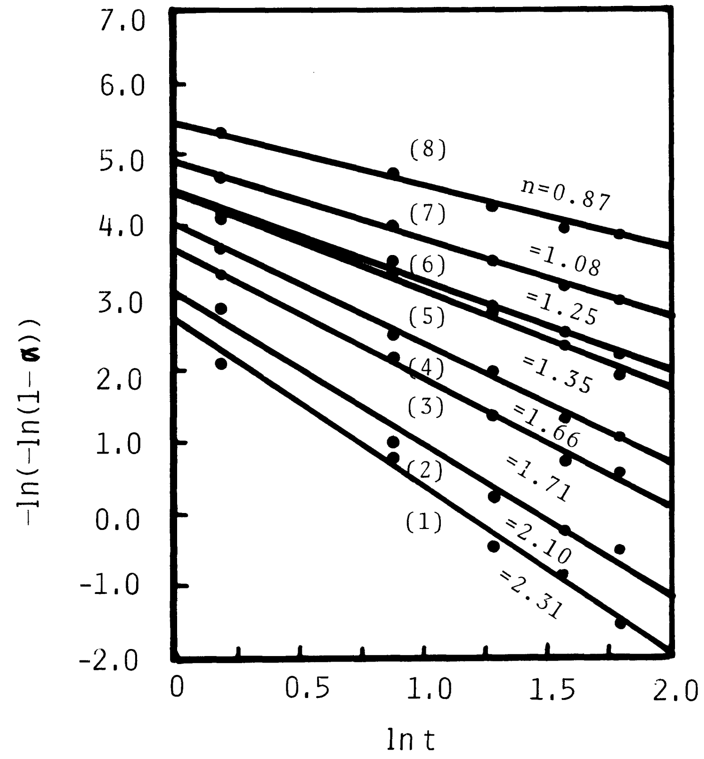

Fig. 2. $-\ln(-\ln(1-\alpha))$-ln t plot of Type I. (1); 101°C, (2);152°C, (3);194°C, (4);238°C, (5); 297°C, (6);349°C, (7);398°C, and (8);446°C.

signals were detected by a home built pulsed NMR spectrometer operating at 11 MHz, and the signals were integrated and averaged by an averager to improve the signal to noise ratio. The spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 were measured at room temperature. T_1 was measured by using the 90^o-$(90^o-\tau)_n$ pulse sequence and T_2 was estimated by FID. The values of T_1 are 162 and 165 ms in the untreated and treated samples, respectively. The shapes of FID in both samples are almost the same except for their magnitude and their decay were nearly exponential. The values of T_2 are 37 and 38 μs in the untreated and treated samples, respectively. These results suggest that there is no difference between the behaviors of protons in both samples and that the environments surrounding the protons do not change throughout the treating at 350^oC.

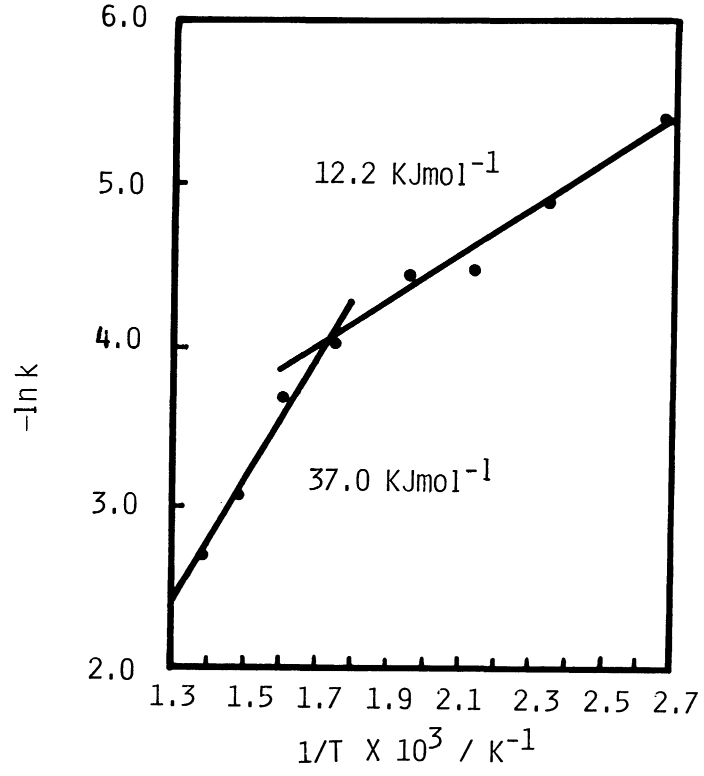

Fig. 3. Arrhenius plot of Type I.

Considering the results mentioned above; (i) the dimension n varies from 0.87 to 2.31 with the increase in heating temperature, (ii) the activation energy shows the crease at about 330^oC, (iii) the gas eliminated by dehydrogenation is only H_2O at all reaction temperatures, and (iv) there is no difference between the behaviors of protons in the untreated and treated samples, it is suggested that there are at least two kinds of processes of Type I. One is the low-temperature process that the atomic hydrogens in the bronze react with the lattice oxygens and H_2O is eliminated, but the bronze keeps its crystal structure with the phase limit. The other is attributed to the high-temperature process that the bronze with the phase limit transforms to MoO_3*, the non-stoichiometric compound with the MoO_3 structure, by elimination of H_2O. In this case, since Avrami-Erofe'ev equation with n=2 is applied, rapid nucleation is followed by two dimentional growth.

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