In-Situ Kinetic Study of Hydrogen Reduction of Fe₂O₃ for the Production of Fe Nanopowder

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The reduction kinetics of Fe₂O₃ nanopowder was investigated by monitoring the reduction behavior in real-time and measuring the amount of outflowing water vapor using *in-situ* hygrometry study. The kinetics of hydrogen reduction of Fe₂O₃ was also studied on the basis of phase transformation, structure modification and outflowing diffusion of water vapor of the Fe₂O₃ powder during reaction. Activation energy for the hydrogen reduction of Fe₂O₃ nanopowder was calculated at various heating rate conditions and conversion fraction of reaction. The activation energies for reduction of Fe₂O₃ nanopowder obtained in this study existed in the range of 20–46 kJ/mol. The activation energy for reduction of Fe₂O₃ nanopowder obtained in this study decreased from 46 kJ/mol to 20 kJ/mol during the entire reduction process. Therefore, the hygrometry study is a powerful tool for *in-situ* kinetic study of hydrogen reduction of metal oxide for mass production.

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1. Introduction

The hydrogen reduction technique has been widely used to fabricate nano-sized metal powder from metal oxide powder.^{1,2)} It is essential to optimize the hydrogen reduction process in order to produce nanopowder with controlled powder characteristics.^{2,3)} Lee and his colleagues have reported that the hydrogen reduction behavior of NiO nanopowder proceeds in a two-step process consisting of a chemical reaction and a subsequent diffusion controlled reaction.⁴⁾ Namely, the agglomerates consisting of nanosized oxide powder finally bring about a diffusion controlled reaction during the hydrogen reduction process. Therefore, it can be thought that the properties of reduced powder are strongly influenced by the reduction mechanism. The Ni powder was selected as a candidate material in the above research based on its phase stability in air atmosphere. Also, the apparent activation energy (Q) was estimated during isothermal reduction process. Consequently, it was finalized that the characteristics of nanosized metal powder product is controllable, relying on the reduction mechanism during the hydrogen reduction process.

On the basis of the above results, in this study, the kinetics at a focused moment was evaluated in real-time through a whole reduction process. Lee and his colleagues reported that the reduction kinetics of Fe₂O₃-NiO for mass production can be evaluated by the real-time hygrometry study.⁵⁾ However, it was found that water vapor trapped in the reactor strongly affected to the outflow rate of water vapor. Hence, the authors carried out a hydrogen reduction experiment using a Fe₂O₃ powder sample of 50 mg to find a method in the sense of the reduction/removal of the retarded water vapor in the reactor. Then, activation energy (Q) is calculated to be compared to the previously reported calculation results. However, unfortunately, the microstructure of reduced powder sample was not observed from vigorous oxidation of the Fe nanopowder in air atmosphere. Therefore, the authors concen-

trated on the evaluation of reduction kinetics based on the activation energy (Q) from hygrometry study.

2. Estimation of Hydrogen Reduction Kinetics

In the kinetic analysis, a reaction progress expresses conventionally in terms of conversion fraction of reaction (α) as

$$\alpha = \frac{\omega_i - \omega}{\omega_i - \omega_f} \quad (1)$$

where ω_i , ω and ω_f are the initial, actual and final weight of the sample, respectively. In other words, the initial and the final weight correspond to the sample weight before and after the reaction, and that is the actual weight at any conversion fraction of reaction during reaction.

The rate of a solid state reaction can be described by

$$\frac{d\alpha}{dt} = \Phi \frac{d\alpha}{dT} = k(T)f(\alpha) = A \exp\left(\frac{-Q}{RT}\right)f(\alpha) \quad (2)$$

where α , $k(T)$, $f(\alpha)$ and Φ is conversion fraction of reaction, the rate constant at temperature T , a function of α representing the reaction mechanism and the heating rate, respectively. And A and Q corresponds to the pre-exponential and activation energy, respectively.

The isoconversional methods calculate the kinetics parameters at a progressive conversion fraction of reaction without modelistic assumptions. Among the isoconversional methods, Kissinger-Akahira-Sunose (KAS) method^{6,7)} has been widely used to estimate activation energy (Q) regardless of the rate expressions of reaction as follows:

$$\ln\left(\frac{\Phi}{T^2}\right) = -\frac{Q}{RT} + \ln\left(\frac{AQ}{g(\alpha)R}\right) \quad (3a)$$

where T is the temperature at an equivalent (fixed) state of transformation and $g(\alpha)$ is the form of eq. (2)'s integral. The $\ln(AQ/g(\alpha)R)$ term is a parameter that is independent of T and Φ . For $\alpha = \text{const.}$, the plot $\ln(\Phi/T^2)$ versus $1/T$ obtained from curves recorded at several heating rates, should be a

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straight line whose slope can be used to calculate the activation energy (Q).

During the reduction of metal oxide powder, metal ions are separated from the oxide by a gas stream containing hydrogen gas, which forms a water vapor as a product during reduction. Using this concept, we can define the conversion fraction of reaction in real-time through a measurement of the outflowing rate of water vapor. From eq. (3a), we can obtain eq. (3b)

$$\ln\left(\frac{\Phi}{T_\alpha^2}\right) = -\frac{Q}{RT_\alpha} + \ln\left(\frac{AQ}{g(\alpha)R}\right) \quad (3b)$$

where, T_α is the temperature at any conversion fraction of reaction. T_α can be determined by graphical method as schematically seen in Fig. 1. For this, the conversion fraction of reaction (α) is obtained by calculating the relative area of the actual reduction reaction with respect to the total reduction process under hygrometry curve (Fig. 1). It is here noted that the baseline for calculation of total area under hygrometry curve can be established by drawing a tangent line at initial and final positions of the curve. In the present study, the total area under a whole hygrometry curve was divided into 10 parts which correspond to 10% of reduction percentage, respectively. This means that the hydrogen reduction process can be estimated periodically by an experimental kinetics study using hygrometry.

The conversion fraction of reaction (α) can be described by:

Fig. 1 The method to obtain the conversion fraction of reaction (α) from hygrometry curves (10 K/min) during hydrogen reduction of ball-milled nanopowder.

$$\alpha = \frac{A_\alpha}{A_t} \quad (4)$$

where A_t is the total area under a whole hygrometry curve and A_α is the area at any conversion fraction of reaction reduction under the hygrometry curve, respectively.

3. Experimental

α -Fe₂O₃ nanopowder was prepared by ball-milling of α -Fe₂O₃ (99.9%, 1 μ m) powder. Ball-milling was carried out in a stainless steel attritor, at a speed of 300 r.p.m. for 10 h. The powder-to-ball mass ratio was 1 : 50 with a powder mass of 100 g and methyl alcohol was used as a process control agent. Ball-milled powder was dried at 333 K for 12 h and sieved down to 150 μ m particle diameter (sieve size, 100 mesh).

Figure 2 shows the SEM (scanning electron microscope) morphology of agglomerated nanopowders of Fe₂O₃ in which the agglomerate with a size range of 5~30 μ m consists of oxide nanoparticles (20~50 nm). X-ray diffraction pattern in Fig. 3 reveals that the ball-milled Fe₂O₃ nanopowder has only α -Fe₂O₃ phase. The XRD pattern was obtained by Rigaku Rotaflex D/MAX system using Cu K_α radiation ($\lambda = 0.15406$ nm) as a target. The mean crystallite size of the Fe₂O₃ nanopowder was 23 nm from the calculation using Scherrer formula based upon the XRD result.⁸⁾ Also, the pore structure of Fe₂O₃ nanopowder was investigated by BET (Brunauer-Emmett-Teller) analysis, the result of which showed that the nanopowder is characteristic of bimodal-typed pore size distribution below 100 nm as shown in Fig. 4. The initial specific surface area of Fe₂O₃ nanopowder used in this experiment was tremendously large with 36 m²/g.

As seen in Fig. 5, the hydrogen reduction behavior was traced by means of measuring the outflowing water vapor from the vertical type furnace using a hygrometry measurement system that is directly connected to the outlet of the furnace. Thus, the water vapor exhausted from a reduction furnace is directly delivered to the humidity sensor of the hygrometry system in which the sensor is the capacitive thin film polymer type (Transmitter: VAISALA HMI 36, Sensor: VAISALA HMP 36E). Humidity measurement is based on the capacitive thin film polymer sensor, and the humidity sensor is located at the tip of the probe. In this study, a 50 ± 5 mg sample of Fe₂O₃ nanopowder was used for the

Fig. 2 SEM micrographs of ball-milled Fe₂O₃ nanopowder for 10 h at: (a) low magnification and (b) high magnification.

Fig. 3 XRD pattern of Fe_2O_3 nanopowder ball-milled for 10 h.

Fig. 4 Pore size distribution of Fe_2O_3 nanopowder ball-milled for 10 h.

Fig. 5 Schematic diagram of the vertical type furnace for hydrogen reduction experiment.

experiment which was conducted in a hydrogen atmosphere under nonisothermal heating conditions with various heating rates of 5, 7, 10, 12 and 15 K/min, respectively. The vertical type furnace comprised of a quartz reaction tube mounted vertically inside a tungsten lamp furnace. A small top-loading alumina crucible was used as a container mounted on an alumina pole. A shallow alumina crucible of 4.5 mm in diameter and 4 mm in height was used as the container to hold the oxide powder bed during the reaction. The powder bed was positioned in the uniform temperature zone of the furnace. Before heating, the furnace tube was evacuated and then flushed with argon gas. The powder sample was heated in a constant hydrogen gas flow (0.151/min) to avoid depletion of the reactant gas during the reaction. The humidity level during the reaction was continuously checked every 5 seconds.

The kinetic parameters for calculating quantitative reduction kinetics were obtained from experimental results of hygrometry curves for various heating rates. Activation energy for hydrogen reduction of Fe_2O_3 nanopowder was then calculated by plotting the parameters in an Arrhenius relation on the basis of the estimation procedure of the reduction kinetics described above.

4. Results

Figure 6 shows the result of a hygrometry study for hydrogen reduction of Fe_2O_3 nanopowder (50 ± 5 mg) during the heating up stage with various heating rates. It is seen that all hygrometry curves for all heating rate conditions unanimously have a single modal curve. As the heating rate increases, the entire reduction process takes place retardedly, namely in which the reduction process gradually starts and ends up at higher temperature. It is reasonable that the reduction kinetics of hydrogen reduction process in this study strongly depends on the heating rate. This is because the lower heating rate provides a kinetic condition for reduction reaction enough compared to the higher rate.

Based on the concept for evaluation of the conversion fraction of reaction in eq. (4) and Fig. 1, we determined the reaction temperature corresponding to each reduction step, T_α from the area of hygrometry curves. As described above, the conversion fraction of reduction reaction is verified by measuring the area of the hygrometry curve during the process assuming that the total area corresponding to complete reduction (100%). By using the data of measured

Fig. 6 Hydrogen reduction behavior of ball-milled Fe₂O₃ nanopowder represented by hygrometry curves.

Table 1 The values of T_α , $\ln(\Phi/T_\alpha^2)$ obtained from hygrometry curves at various conversion fraction of reaction (α) and heating rate (Φ) conditions during hydrogen reduction.

	α	Φ				
		5 K/min	7 K/min	10 K/min	12 K/min	15 K/min
T_α (K)	0.1	594.3	615.3	631.2	646.0	658.1
	0.2	620.4	642.1	662.1	676.9	692.7
	0.3	638.3	660.8	682.1	698.9	716.7
	0.4	653.3	676.0	700.4	717.8	738.0
	0.5	666.2	689.4	716.2	734.9	758.0
	0.6	678.3	702.8	732.0	750.8	776.7
	0.7	690.4	715.6	749.9	767.9	795.5
	0.8	703.3	729.6	763.7	784.8	815.4
	0.9	721.6	752.9	800.4	822.8	874.1
	1.0	763.7	807.2	873.7	909.8	965.3
$\ln(\Phi/T_\alpha^2)$	0.1	-11.165	-10.898	-10.593	-10.457	-10.271
	0.2	-11.251	-10.984	-10.688	-10.550	-10.373
	0.3	-11.308	-11.041	-10.748	-10.614	-10.441
	0.4	-11.355	-11.086	-10.801	-10.668	-10.500
	0.5	-11.394	-11.126	-10.845	-10.715	-10.553
	0.6	-11.430	-11.164	-10.889	-10.758	-10.602
	0.7	-11.465	-11.200	-10.932	-10.802	-10.650
	0.8	-11.502	-11.239	-10.974	-10.846	-10.699
	0.9	-11.554	-11.302	-11.068	-10.941	-10.838
	1.0	-11.667	-11.441	-11.243	-11.142	-11.037

temperatures from the results of Fig. 6, the corresponding values of $\ln(\Phi/T_\alpha^2)$ for various heating rates were calculated and summarized in Table 1.

On the basis of the data in Table 1, the kinetics for hydrogen reduction process depending on conversion fraction of reaction was investigated in terms of an effective activation energy for hydrogen reduction process. Figure 7 represents the temperature dependence of reduction process in the relationship of $\ln(\Phi/T_\alpha^2)$ versus $1/T_\alpha$ for various conversion fraction of reaction from $\alpha = 0.1$ to 1.0 (Fig. 6). As a result, all slopes look similar at every condition below $\alpha = 0.8$, but the slopes above $\alpha = 0.8$ changed remarkably. Based on these data, we calculated an effective activation

Fig. 7 $\ln(\Phi/T_\alpha^2)$ vs. $1/T_\alpha$ graph obtained from hygrometry curves at varying conversion fraction of reaction (α) and heating rate (Φ).

Fig. 8 The activation energies for hydrogen reduction of Fe₂O₃ nanopowder from hygrometry curves, represented as a function of conversion fraction of reaction (α).

energy from the slope of the arrhenius relation for α values and plotted them in Fig. 8. From this result, it was convinced that there might be negligible change in the pore structure as well as related surface area of the powder, consequently resulting in no increase of activation energy. As seen in the result of Fig. 8, the activation energy for hydrogen reduction process of Fe₂O₃ nanopowder varies in the range from 20 to 46 kJ/mol depending on conversion fraction of reaction. Initially, it decreased slightly from 46 kJ/mol to 35 kJ/mol until α reached 0.8 and then it was abruptly fell to 20 kJ/mol beneath $\alpha = 0.8$.

5. Discussion

It is interesting that the hydrogen reduction kinetics of nanoscale Fe_2O_3 powder depends strongly on the degree of reduction process (α). Moreover, it is unexpectedly surprising that the gradual decrease of activation energy with increasing α became larger in the final stage of the reduction process beyond $\alpha = 0.8$. Regarding this unusual reduction behavior there can be two possible factors affecting the kinetics of hydrogen reduction process of nanoscale metal oxide powder. One is the phase transformation of iron oxide occurring during reduction process and the other is the structural modification of reduced metal oxide powder such as pore structure change by sintering of the surface of reduced powder agglomerates.

5.1 Phase transformation effect

As far as the phase transformation of iron oxide during reduction process is concerned, two major reduction steps of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ can be considered. These reactions can occur simultaneously in the process of reduction of iron oxide powders. Therefore we obtain an effective activation energy for intermediate stage of reduction process including a mixed type of reduction processes. According to literature data on the activation energy for the reduction of Fe_2O_3 at each step,^{9–19)} both reactions have a wide range of activation energies. In other words, the activation energy for $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step and $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ step exists in the range of 75–245 kJ/mol and 15–172 kJ/mol, respectively. Thus, it is thought that the reduction step for initial stage ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$) demands a higher activation energy than that of $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ step. When Fe_2O_3 is reduced to Fe_3O_4 , oxygen concentration is reduced by approximately 12%. In this case, we can predict that the α value is in the range of 0–0.2. In the present study, it was very difficult to confirm the sequence of reduction process of iron oxide by phase analysis using X-ray diffraction study. This is mostly attributed to explosive oxidation of the reduced Fe nanopowder. However, we found interesting evidences on simultaneous reduction reaction from the plateaus near low temperatures (580 K–640 K) in Fig. 6. Assuming that such 12% weight loss due to the reaction of Fe_2O_3 - Fe_3O_4 is converted to the relating reduction process of $\alpha = 12\%$, it is found that the corresponding temperature to such α value is near 623 K at which the plateaus in the hygrometry curve appears. In this respect, it is recognized that the reduction reaction of iron oxide occurs simultaneously from Fe_2O_3 to Fe. Earlier investigations also reported on the occurrence of simultaneous reduction process of iron oxide.^{20–22)}

In subsequent reaction to the completion of reduction, the $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ reduction can be taken as a major reaction leading the whole reduction process. However, it should be noted that other reduction reactions such as $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ and $\text{FeO} \rightarrow \text{Fe}$ affecting α value probably occur simultaneously in the intermediate stage depending on the oxygen concentration. In this case no specific reaction leads total process dominantly so that there is no large variation in activation energy. Such a mixed type reduction process might be responsible for a slight decrease of activation energy against α value below $\alpha = 0.8$, as shown in Fig. 8.

5.2 Effect of structure modification

There is still a question regarding abrupt decrease of activation energy beyond $\alpha = 0.8$ (i.e. $0.9 \leq \alpha \leq 1.0$). It seems problematic to understand this unusual behavior only in terms of phase transformation effect. One possible reason for that can result from the change of reduction mechanism due to structure modification in powder agglomerates by surface sintering effect. That is, as the reduction of the oxide powders proceeds completely, the surface region consisting of fully reduced nanopowders undergoes a rapid sintering which leads to pore elimination in the surface. Such structure modification in the surface region remarkably influences diffusion process of reacting gas as H_2 and H_2O , as a consequence causing the change of rate controlling kinetics in reduction process, for example, from a chemical reaction controlling process to a diffusion controlling one. This implies that the out-diffusion process of water vapor molecules through a dense sintered surface dominates the rate of further reduction process in the residual oxide powder.

According to the previous study on hydrogen reduction of NiO nanopowder,⁴⁾ the reduction of NiO nanopowder proceeds in a two-step process consisting of a chemical reaction and a subsequent diffusion controlled reaction. The isothermal reduction at higher temperature resulted in the decrease of pore volume and the change of pore size distribution, causing the change of reduction mechanism from chemical reaction to diffusion controlled reaction. The latter kinetic process by a diffusion control due to the sintering effect of reduced Ni nanopowder in the surface region of the sample led to an increase in activation energy for isothermal reduction process. Especially, the nanopowder sintering on the agglomerate surface region was mostly responsible for the closure of pore channel for out-diffusion of water vapor. It implies that the reduction is gradually retarded by a diffusion controlling kinetic process as the surface region of the powder becomes dense. In addition, a bimodal type of humidity curve was obtained, which represents the interplay of two reaction rate controlling kinetics as chemical reaction and diffusion reaction. However, the hygrometry curves from this study show a single-modal type. Being different from the case of NiO showing a bimodal type curve, this study represented a single modal curve which is characterized by dominant role of chemical reaction control. Therefore, this finding is quite different from the previous study. From this result, it was convinced that there might be negligible change in the pore structure as well as related surface area of the powder, consequently resulting in no increase of activation energy. This is because the activation energy in the present investigation was rather lowered. Thus, a drop of activation energy in the final stage of reduction is believed not to result from the change of reduction mechanism due to structure modification of the agglomerate powder. This interpretation is supported by our previous investigation on the activation energy for Fe_2O_3 reduction obtained from DTG curve.²³⁾ It was found the values of activation energy remained almost constant in the whole range of reduction process. The average activation energy in the whole range of reduction amounts to about 40 kJ/mol which corresponds to that of chemical reaction mechanism. Also, it is confirmed that the activation energies

in the range of $\alpha < 0.8$ having almost equal values are consistent with those of literature values.^{24,25)}

5.3 Retarding effect of outflowing diffusion of water vapor

Now the question arises how and what we can understand about the results (Fig. 8) of a hygrometry study for understanding the hydrogen reduction of process of nanoscale Fe₂O₃ powder. Before discussing this issue, it should be noted that the hygrometry study is an indirect experimental tool for analysis of the hydrogen reduction process through the measurement of removal rate of a water vapor as a product during reduction reaction.

From hygrometry study for hydrogen reduction of massive nanoscale Fe₂O₃ powder, it was recently observed that considerable retardation occurred in the final stage of the reduction process.⁵⁾ Trap of water vapor inside the reactor was interpreted to be responsible for the retardation of water vapor outflow. This points out that the completion of reduction reaction measured by hygrometry study can be retarded in the shifted form in the hygrometry curve into higher temperatures compared to the case of the TG measurement. This argument becomes clear in Fig. 9, which compares the present hygrometry curve for reduction behavior of Fe₂O₃-NiO nanopowder with that of DTG curve obtained under the same condition (27 K/min).⁵⁾ Such a phenomenon is believed to mainly appear in the conditions of unbalanced gas flow during the reduction process. For example, as the reduction process progresses, a large amount of water vapor tends to be accumulated at the outlet zone of the reactor when outflow of water vapor from the reactor does not follow a mass balancing condition. Thus, under this circumstance, the rate controlling step of reduction process can be regarded as out-diffusion process of water vapor regardless of completion of true reduction reaction in the oxide sample. Consequently, it results in retardation of reduction process especially in the final stage of the process. In other words, the retardation of reduction process enables us misunderstand that the reduction reaction is still going on even in case of the completion of the reduction process. This is basically a decisive difference in both methodologies for studying a hydrogen reduction kinetic for metal oxide.

Fig. 9 Hydrogen reduction behavior of ball-milled Fe₂O₃-NiO powder represented by DTG and hygrometry curves (27 K/min).⁵⁾

Fig. 10 Experimental diffusion coefficients (H₂-H₂O).²⁶⁾

Now it is important to understand the influence of out-diffusion of water vapor on the whole reduction kinetics in terms of Q value. Therefore, we estimated and calculated the activation energy for diffusion process of H₂-H₂O gas mixture based upon the literature data.²⁶⁾ The result is represented in an Arrhenius plot in Fig. 10. Also, the activation energy for H₂-H₂O diffusion from Fig. 10 is calculated to be about 4 kJ/mol. This Q value for H₂-H₂O diffusion is too low compared to those for reduction process obtained in this study. However, such a low activation energy predominates when out-diffusion of water vapor in the reactor apparently appears to control the rate of a whole reduction process. In this case, the reduction kinetics controlled by out-diffusion process of a H₂-H₂O mixed gas is thought to give rise to the drop in activation energy in the final stage of the reduction process, for instance, in the range of $0.9 \leq \alpha \leq 1.0$. This means that the removal process of residual water vapor in the reactor outside the reactor even after completion of reduction can prevail a reduction kinetics as a controlling step as depicted in Fig. 9. In this respect it is noted that the analysis of hydrogen reduction kinetics by hygrometry study provides reliable data for early stage of the process in the range of $0.1 \leq \alpha \leq 0.8$ in the present investigation. Compared with the reported data for hydrogen reduction process of Fe₂O₃-Fe (51 kJ/mol at <848 K,²⁴⁾ 38 kJ/mol at >848 K²⁴⁾ and 57 kJ/mol²⁵⁾, the present data of 35–46 kJ/mol obtained in this study is reliable. Especially, we expect that the initial activation energy at $\alpha = 0.1$ is most accurate corresponding to real value. In order to check this point, isothermal reduction kinetics experiment for the same powder samples is on-going and the result will be reported in near future.

Based upon the explanations discussed above, thus, it is concluded that the hygrometry study during hydrogen reduction system can be effectively applied to investigate the reduction kinetics for mass production as a new method.

6. Conclusion

In the present study the synthesis and related kinetics of Fe nanopowder by hydrogen reduction of Fe_2O_3 were investigated by a reduction kinetics experiment using hygrometry in real-time. The ball-milled Fe_2O_3 agglomerate powder of 20~50 nm in grain size, was used for this study. Activation energy for Fe_2O_3 reduction showed that initially it decreased slightly from 46 kJ/mol to 35 kJ/mol until α reached 0.8 and then it was abruptly lowered to 20 kJ/mol beneath $\alpha = 0.8$. In this study, it was found that the activation energy in the range of $0.1 \leq \alpha \leq 0.8$ decreased slightly due to the change of activation energy with the phase transformation. Also, the activation energy in the range of $0.9 \leq \alpha \leq 1.0$ decreased dramatically, because the residual water vapor in the reactor was not removed after completed reduction. The activation energies obtained from the hygrometry curve seem reasonable to exist approximately in the range of reported data for the hydrogen reduction process in a number of previous works. Thus, it is thought that the activation energy values calculated at initial and intermediate stage ($0.1 \leq \alpha \leq 0.8$) of reaction from hygrometry curves are reasonable. Consequently, the hygrometry study during hydrogen reduction system can be applied to investigate the reduction kinetics for mass production as a new method.

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