Kinetic Study on the Hydrogen-Oxygen Reaction over the Manganese Oxide Catalyst

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Abstract We investigated the method to remove trace oxygen in vary gases by using the oxidation of manganese(II) oxide.

This reaction achieved under the normal temperature and pressure, oxygen removal capacity by the oxidation of manganese(II) oxide was closely related with the reduction process of manganese(II) oxide by hydrogen[1, 2, 5].

By the oxidation process of manganese(II) oxide under the normal temperature and its reduction by hydrogen at 450℃, it is a question of the hydrogen-oxygen reaction by hydrogenation of oxygen.

Kinetic study on the hydrogen-oxygen reaction over Mn_xO_y-rare earth oxide-clay catalyst was investigated.

Key words manganese, oxygen removal, kinetic study

Introduction

The great leader Comrade **Kim Jong Il** said as follows.

"Now is the age of science and technology, and unprecedently fast speed is the major characteristic of the development of modern science and technology."
("**KIM JONG IL** SELECTED WORKS" Vol. 12 P. 199)

To purify of various kinds of gas, such as hydrogen, nitrogen and argon, is a pressing problem in many domains of national economy including electric automation industry, production of pure metals and high purity material synthesis.

To remove impurity oxygen is important before anything else in purifying of various kinds of gas.

Because production of such raw gases is based on separating of corresponding elements in air and it is unavoidable saturation of air in its saving and handling.

In the preceding study, there are two methods for oxygen removal－method using the oxidation of metal and metal oxide, and removal with the water by hydrogenation of oxygen using precious metal or transition metal catalyst.

In general, it has been known to kinetically consider the hydrogen-oxygen reaction over the precious metal or transition metal catalyst[2－4, 6－10], but not almost using manganese

series as catalyst.

In this paper, kinetic study on the hydrogen-oxygen reaction over the Mn_xO_y-rare earth oxide-clay catalyst that has the most capacity for oxygen removal was investigated.

1. Kinetic Consideration by Variation of the Partial Pressure Ratio of Hydrogen and Oxygen

The hydrogen-oxygen reaction, that is our attention, is a comparatively simple reaction that the starting materials are oxygen and hydrogen, its rate question of reaction can be described as follows under the certain conditions.

$$w = k \cdot P_{O_2}^n \cdot P_{H_2}^m \tag{1}$$

After indicating the reaction rate by differential expression of x_{O_2}, variation rate of oxygen as a function of contact time, when it has given the initial reaction rate we can attained the following equation.

$$w_0' = k(P_{O_2})_0^{n-1} \cdot (P_{H_2})_0^m \tag{2}$$

When giving a natural logarithm at both sides above, the equation is as follows.

$$\ln w_0' = \ln k + (n-1)\ln(P_{O_2})_0 + m\ln(P_{H_2})_0 \tag{3}$$

If we can measure w_0' by changing of initial partial pressure of hydrogen under the certain initial partial pressure of oxygen, it could be obtained the relation as follows.

$$\ln w_0' = m\ln(P_{H_2})_0 + \text{const} \tag{4}$$

And then, as giving variety of $(P_{O_2})_0$ under the certain initial partial pressure of hydrogen, the following relation is obtained.

$$\ln w_0' = (n-1)\ln(P_{O_2})_0 + \text{const} \tag{5}$$

On the other hand, when w_0' is measured with changing temperature under the certain initial partial pressures of oxygen and hydrogen, we can obtain the following relation from Arrhenius equation.

$$\ln w_0' = -\frac{E^{\neq}}{R}\frac{1}{T} + \text{const}$$

We can attain m, n and $E^{\neq}$ from presuming regression coefficients of such regression models.

2. Experimental Method

Kinetic experiment was made with considering the variation rate of oxygen, according to analysis of oxygen concentration of input and output with gas-chromatography （"GC-4B"） after putting up 1mL of catalyst in the flow type fixed layer reactor.

Reaction gas was diluted to corresponding partial pressure after adjusting the ratio of oxygen and hydrogen.

Firstly the variation rate of oxygen was measured as a function of contact time with changing of $(P_{O_2})_0/(P_{H_2})_0$ at 180 ℃ for determination of the order of reaction to hydrogen and oxygen(Fig. 1).
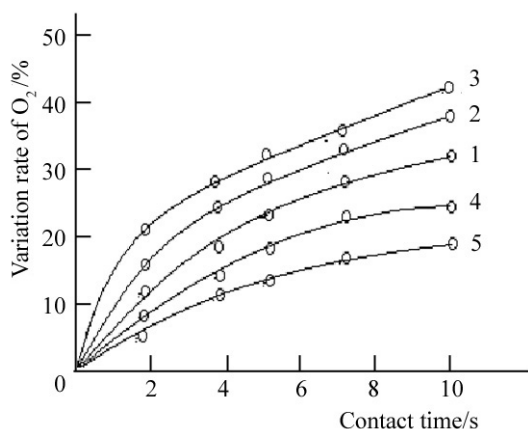

Fig. 1. Variation rate of oxygen according to contact time
under the different ratio $(P_{O_2})_0/(P_{H_2})_0$

1－5 is ratio $(P_{O_2})_0/(P_{H_2})_0$ 1/1, 1/1.5, 1/2, 1.5/1, 2/1 reaction temperature 180℃

According to the previous study[1], we selected the suitable kinetic equation for the experimental curve, by its formula, determined values for a and b(table 1). As we consider the physical meaning, $1/b$ is initial rate.

Fig. 2 shows the variation of initial reaction rate as a function of variety of $(P_{O_2})_0$ and $(P_{H_2})_0$, obtained from data in table 1.

Table 1. Results of empirical formula $y=t/(b+at)$ indicating
kinetic curve(reaction temperature: 180℃)

$(P_{O_2})_0/(P_{H_2})_0$	a	b	Standard deviation	$W_0=1/b$
1.0/2.0	1.905	5.32	$3.00 \cdot 10^{-4}$	0.188 0
1.0/1.5	1.760	8.70	$2.23 \cdot 10^{-3}$	0.155 0
1.0/1.0	1.668	12.30	$5.25 \cdot 10^{-4}$	0.081 3
1.5/1.0	1.301	23.50	$3.29 \cdot 10^{-4}$	0.042 6
2.0/1.0	0.732	31.50	$7.80 \cdot 10^{-5}$	0.031 7

As shown in Fig. 2, the reaction rate is increased with increasing of the partial pressure of hydrogen and decreased with oxygen partial pressure. That is, the order of reaction for hydrogen is plus, minus for oxygen.

Fig. 3 shows variation rate of oxygen as a function of contact time under the different temperature with fixing ratio $(P_{O_2})_0/(P_{H_2})_0$.
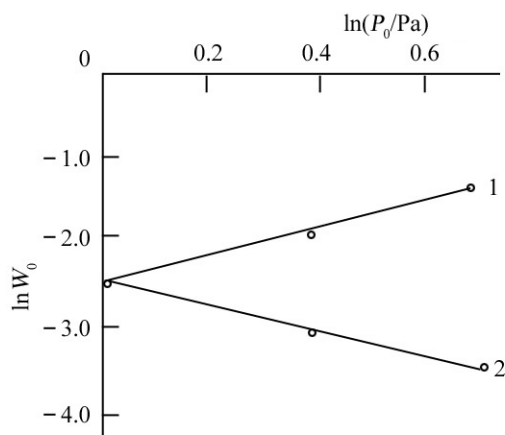

Fig. 2. Initial reaction rate variation curve of the reaction producing water as a function of variety of $(P_{O_2})_0$ and $(P_{H_2})_0$
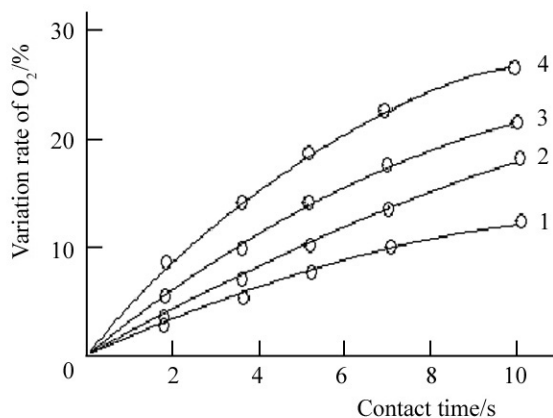1—H_2, 2—O_2

Fig. 3. Variation rate curves of oxygen as a function of contact time at the different reaction temperature
1—150℃, 2—160℃, 3—170℃, 4—180℃
$(P_{O_2})_0/(P_{H_2})_0$　1.5

From that we could obtain the apparent activation energy for this reaction. The results that determined the empirical formula describing kinetic curves above are the same as table 2.

Table 2. a, b and initial rate of the kinetic curve equation, $y = t/(b + at)$ under the different temperature.($(P_{O_2})_0/(P_{H_2})_0$　1.5)

Reaction temperature/K	a	b/s	Standard deviation	$W_0 = 1/b$
423	1.95	55.4	$0.889 \cdot 10^{-4}$	0.018 1
433	1.21	44.2	$4.340 \cdot 10^{-4}$	0.022 6
443	1.16	29.4	$4.720 \cdot 10^{-4}$	0.033 0
453	1.30	23.5	$3.290 \cdot 10^{-4}$	0.042 6

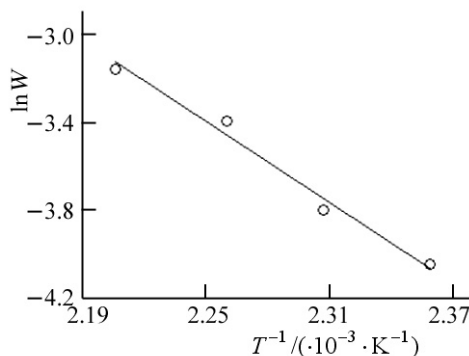From above data, we could obtain such the relation $\ln W_0 \sim 1/T$ as Fig. 4.

Fig. 4. The relation $\ln W \sim 1/T$　$(P_{O_2})_0/(P_{H_2})_0$　1.5

From the gradient of linear equation above, the apparent activation energy $E^{\neq}$ is 27.63kJ/mol.

3. The Mechanism of the Hydrogen-Oxygen Reaction over the Manganese Oxide(Mn_xO_y) Catalyst

We have brought out the mechanism for the hydrogen-oxygen reaction over the catalyst based on prior kinetic experiment.

By our study, the order related to the initial reactant can not be negative at any conditions in adsorption-collision mechanism, while it can be negative in adsorption-adsorption mechanism. Therefore it presumes that this kinetic experimental result can be performed as adsorption-adsorption mechanism. To confirm it, we made following experiment and then considered its mechanism.

Above all black catalyst was filled in reaction tower and passed nitrogen gas. With increasing of temperature from 250℃ to 450℃ as an interval of 100℃ and maintaining for one hour at each temperature, the color change was observed.

It was observed that the color changed in dark brown after an hour at 250℃, in dark grey at 350℃ and in greenish gray at 450℃. Changing color of the catalyst from black to greenish gray in flowing of inert gas nitrogen suggest that the dissociation of oxygen arise as consequence of the process of $Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ with increasing of temperature over the catalyst layer.

And then by empirical data that we obtained, even though the catalyst was reduced for a long time at 250℃ in reducing process of catalyst by hydrogen, color of the catalyst only changed in gray.

Through such experimental and empirical data, physical property for manganese oxide, we guess that the catalyst for the hydrogen-oxygen reaction is intermediate between Mn_3O_4 and Mn_2O_3 and such state can be as a transient state composing from dissociation adsorption of oxygen to Mn_3O_4. We are going to express as Mn_xO_y such state and consider the mechanism for such reaction with supposing it as an activation center of catalyst at the hydrogen-oxygen reaction.

And then we have considered the adsorption characteristics of O_2 and H_2 to catalyst Mn_xO_y.

Hydrogen-oxygen reaction over the catalyst is an inhomogeneous catalyst reaction and it has precondition for adsorption of reactants oxygen and hydrogen onto catalyst surface. So adsorption amount data of reactant on the catalyst has a significant as basic data for solution of reaction mechanism.

The experiment was performed with volume calculation method after reaching to adsorption balance, with changing pressure of oxygen and hydrogen at normal temperature and

240°C with high vacuum adsorption equipment. By the experiment at the normal temperature adsorption of oxygen and hydrogen observed hardly but it observed clearly around 200°C.

Fig. 5 shows adsorption isotherm of O_2 and H_2 on the catalyst Mn_xO_y at 240°C.

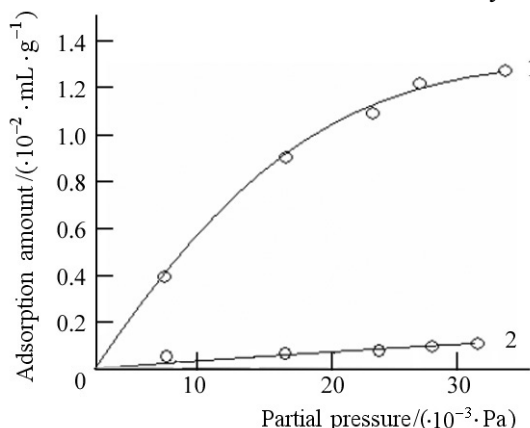Fig. 5. Adsorption curves of hydrogen and oxygen to the manganese oxide.

1$-O_2$, 2$-H_2$

The adsorption amount of O_2 over the Mn_xO_y at 240°C was much above 10 times than thing of H_2 that considered in general range of pressure. This is a reason for difference in the adsorption capacity between O_2 and H_2 over the Mn_xO_y, and it shows that the capacity of oxygen is far large than that of hydrogen.

For clear up the mechanism for the hydrogen-oxygen reaction over the catalyst Mn_xO_y, it made assumption as following from based on such experimental fact.

Firstly, reactants O_2 and H_2, it makes dissociation adsorption on the surface of Mn_xO_y.

Secondly, adsorption process of O_2 and H_2 onto the surface of Mn_xO_y is fast and in balance state actually.
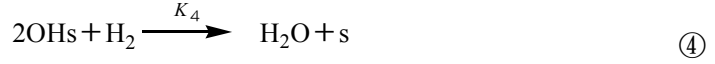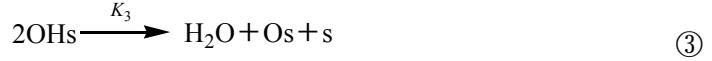
Thirdly, adsorption intensity of oxygen is much large than that of hydrogen and adsorption center of the catalyst surface is saturated approximately by adsorption sorts of oxygen under the reaction condition.

Based on such assumption, the mechanism of reaction producing water by hydrogenation of oxygen on the surface of catalyst Mn_xO_y was considered with adsorption-collision mechanism and adsorption-adsorption mechanism.

4. Adsorption-Collision Mechanism

We can assumption two courses as following related to adsorption-collision mechanism

$$O_2 + 2s \underset{}{\overset{K_1}{\rightleftharpoons}} 2Os \qquad\qquad ①$$

$$2Os + H_2 \underset{}{\overset{K_2}{\rightleftharpoons}} 2OHs \qquad\qquad ②$$

$$2OHs \xrightarrow{K_3} H_2O + Os + s \qquad \text{③}$$

$$2OHs + H_2 \xrightarrow{K_4} H_2O + s \qquad \text{④}$$

First of all kinetic equation for the course producing H_2O through elementary reaction ①, ②, ③, was induced.

$$w = k_3 \theta_{OH}^2, \quad \theta_{OH} = \sqrt{K_2 \cdot P_{H_1}} \cdot \theta_0 \approx \sqrt{K_2 \cdot P_{H_1}}$$

$$\therefore w = k_3 K_2 P_{H_2} = k_{exp} P_{H_2}$$

where $k_{exp} = k_3 K_2$.

At reaction rate equation according to this reaction mechanism, the order of reaction related to P_{H_2} is first order and zero order for P_{O_2}.

And kinetic equation for the course forming H_2O through elementary reaction ①, ②, ④ was induced as follows.

$$w = k_4 \theta_{OH}^2 P_{H_2}, \quad \theta_{OH} = \sqrt{K_2 \cdot P_{H_1}}$$

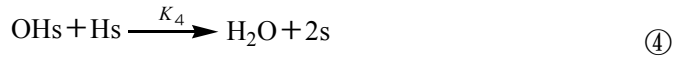$$\therefore w = k_4 K_2 P_{H_2}^2 = k_{exp} P_{H_2}^2$$

where $k_{exp} = k_4 K_2$.

At reaction rate equation according to this reaction mechanism, the order of reaction related to P_{H_2} is second order and zero order for P_{O_2}.

These results does not catch kinetic experimental results that the order of reaction related to P_{H_2} is about first order and -0.5 order for P_{O_2}.

After all this suggest that the mechanism of the hydrogen-oxygen reaction by heterogeneous reaction of hydrogen and oxygen on the surface of catalyst is not adsorption-collision mechanism.

5. Adsorption-Adsorption Mechanism

The elementary reaction can appear as follows.

$$O_2 + 2s \xrightleftharpoons{K_1} 2Os \qquad \text{①}$$

$$H_2 + 2s \xrightleftharpoons{K_2} 2Hs \qquad \text{②}$$

$$2Os + Hs \xrightleftharpoons{K_3} OHs + s \qquad \text{③}$$

$$OHs + Hs \xrightarrow{K_4} H_2O + 2s \qquad \text{④}$$

Because the adsorption intensity of oxygen is very big, we can obtain the following results to adsorption site if $\theta_0 \approx 1$.

$$\theta_s = \frac{\theta_0}{\sqrt{K_1 \cdot P_{O_2}}} \approx \frac{1}{\sqrt{K_1 \cdot P_{O_2}}}$$

$$\theta_{\mathrm{H}} = \sqrt{\frac{K_2 \cdot P_{\mathrm{H}_2}}{K_1 \cdot P_{\mathrm{O}_2}}}$$

$$\theta_{\mathrm{OH}} = K_3 \cdot \sqrt{K_2 \cdot P_{\mathrm{H}_2}}$$

If step ④ is rate determining step, the reaction rate equation is as follows.

$$w = k_4 \theta_{\mathrm{OH}} \theta_{\mathrm{H}} = \frac{k_4 \cdot K_3 \cdot K_2 \cdot P_{\mathrm{H}_2}}{\sqrt{K_1} \cdot P_{\mathrm{O}_2}^{1/2}}$$

$$w = k_{\exp} \cdot P_{\mathrm{H}_2} \cdot P_{\mathrm{O}_2}^{-0.5}$$

where $k_{\exp} = k_4 \cdot k_3 \cdot k_2 \cdot k_1^{-1/2}$.

At reaction rate equation according to this reaction mechanism, the order of reaction related to P_{H_2} is first order and -0.5 order for P_{O_2} and catch satisfactorily above kinetic experimental results.

After all, we can see the hydrogen-oxygen reaction over the catalyst carry out according to adsorption-adsorption mechanism that surface hydroxyl group is formed from between atomicity oxygen formed by dissociation adsorption of oxygen, hydrogen and hydrogen and then water is produced by reaction between this hydroxyl group and another atomicity hydrogen.

Through consideration of kinetic and mechanism on the hydrogenation of oxygen over the catalyst Mn_xO_y, we can obtain the rate equation as follows.

$$w = k \cdot P_{\mathrm{H}_2}^m \cdot P_{\mathrm{O}_2}^n \quad (m \approx 1,\ n \approx -0.5)$$

Conclusion

Through kinetic study on the hydrogen-oxygen reaction over the catalyst Mn_xO_y, we obtained following results.

Firstly, Mn_xO_y-La_2O_3-clay acts as catalyst of the hydrogen-oxygen reaction at 150 °C and over.

Secondly, the rate formula of the hydrogen-oxygen reaction over that catalyst is $w = k \cdot P_{\mathrm{H}_2}^m \cdot P_{\mathrm{O}_2}^n$ and the apparent activation energy is about 26.7kJ/mol.

Thirdly, we can see that the hydrogen-oxygen reaction over that catalyst carry out as adsorption-adsorption mechanism when the ratio of initial partial pressure is 0.5 and over $((P_{\mathrm{O}_2})_0 /(P_{\mathrm{H}_2})_0 \geqq 0.5)$.

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