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PROMOTER ACTION OF POTASSIUM OXIDE IN AMMONIA SYNTHETIC IRON CATALYST

By Akio Kazusaka* and Isamu Toyoshima*

It has been proposed that the rate of ammonia decomposition over ammonia synthetic iron catalysts is controlled by the desorption of adsorbed nitrogen\(^1\). The observation of the stoichiometric number, however, suggested the dehydrogenation step of NH\(_3\)(a), NH\(_2\)(a) or NH(a) to be rate-determining, where (a) denotes the adsorbed state\(^2\).

As to this disagreement, we showed on the basis of kinetics of this reaction that the reaction mechanism may depend upon the reaction temperature\(^3\) and also the content of potassium oxide promoter in ammonia synthetic iron catalyst\(^4\).

In this work the promoter action of potassium oxide in ammonia synthetic iron catalyst was studied by applying the method of stoichiometric number of the rate-determining step \(\nu_r\) to the ammonia decomposition.

The experimental apparatus and procedures were similar to those used in the previous works\(^5,6\). Four kinds of iron catalyst were prepared in the usual method at Government Chemical Industrial Research Institute, Tokyo, and the content of potassium oxide in them was varied from 0 to 1.54 wt % with the fixed amount of alumina as shown in Table 1. Catalyst used was amounted between 0.4 and 1.5 gr. depending on their activity and was from 12 to 20 mesh size.

\(\text{Note}\)

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Catalyst No. & Substance & Total Iron (wt %) & Al\(_2\)O\(_3\) & K\(_2\)O & SiO\(_2\) \\
\hline
1 & Total Iron & 70.47 & 2.69 & - & 0.09 \\
2 & Total Iron & 69.95 & 2.55 & 0.33 & 0.09 \\
3 & Total Iron & 69.41 & 2.53 & 0.58 & 0.15 \\
4 & Total Iron & 67.42 & 2.39 & 1.54 & 0.13 \\
\hline
\end{tabular}
\end{table}

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Promoter Action of Potassium Oxide in Ammonia Synthetic Iron Catalyst

The catalysts were reduced preliminarily at 600°C for 72 hr in a purified hydrogen at a flow rate of 500 cc/min. Decomposition reaction of 15N-enriched ammonia was carried out at 361°C. The reaction gas was a 3:1 mixture of hydrogen and nitrogen besides ca. 15 mmHg 15N-enriched ammonia. The total pressure was kept at 750 mmHg during the reaction. Nitrogen and hydrogen were purified by the same method as described previously.

Table 2 shows the observed results. In the present experimental conditions, three kinds of reaction proceeded concurrently; the ammonia decomposition, the exchange reaction of 15N between ammonia and nitrogen gas, and the nitrogen isotope equilibration reaction.

The forward and backward unidirectional rates, \( V_+ \) and \( V_- \), of ammonia

<table>
<thead>
<tr>
<th>Catalyst No.</th>
<th>( t^* ) (hours)</th>
<th>( P_A ) (mmHg)</th>
<th>( Z^A ) (%)</th>
<th>( Z^{N#} ) (%)</th>
<th>( Z^N ) (%)</th>
<th>( Z^# ) (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>13.58</td>
<td>83.4</td>
<td>82.6</td>
<td>1.71</td>
<td>1.40</td>
</tr>
<tr>
<td>(1.49 gr)</td>
<td>0.97</td>
<td>10.46</td>
<td>79.2</td>
<td>78.8</td>
<td>2.61</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>2.29</td>
<td>7.42</td>
<td>—</td>
<td>68.9</td>
<td>3.44</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>5.62</td>
<td>5.32</td>
<td>35.2</td>
<td>27.3</td>
<td>4.68</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>8.91</td>
<td>5.09</td>
<td>21.1</td>
<td>10.5</td>
<td>5.00</td>
<td>8.10</td>
</tr>
<tr>
<td>2</td>
<td>3.46</td>
<td>13.65</td>
<td>83.1</td>
<td>86.6</td>
<td>1.72</td>
<td>1.65</td>
</tr>
<tr>
<td>(0.42 gr)</td>
<td>14.33</td>
<td>11.20</td>
<td>79.2</td>
<td>79.5</td>
<td>2.47</td>
<td>1.94</td>
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<tr>
<td></td>
<td>35.22</td>
<td>8.09</td>
<td>63.0</td>
<td>64.5</td>
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<tr>
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<td>50.17</td>
<td>7.03</td>
<td>60.9</td>
<td>53.3</td>
<td>4.03</td>
<td>2.91</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>16.23</td>
<td>93.4</td>
<td>96.7</td>
<td>0.478</td>
<td>0.755</td>
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<tr>
<td>(0.52 gr)</td>
<td>0.69</td>
<td>14.60</td>
<td>94.5</td>
<td>95.2</td>
<td>1.06</td>
<td>0.810</td>
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<tr>
<td></td>
<td>2.24</td>
<td>12.36</td>
<td>92.6</td>
<td>92.6</td>
<td>1.69</td>
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<tr>
<td></td>
<td>5.51</td>
<td>8.96</td>
<td>85.2</td>
<td>87.5</td>
<td>2.72</td>
<td>1.06</td>
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<tr>
<td></td>
<td>8.52</td>
<td>6.90</td>
<td>76.3</td>
<td>80.5</td>
<td>3.35</td>
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</tr>
<tr>
<td>4</td>
<td>0</td>
<td>20.18</td>
<td>96.9</td>
<td>—</td>
<td>0.348</td>
<td>0.697</td>
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<tr>
<td>(1.29 gr)</td>
<td>0.72</td>
<td>19.84</td>
<td>97.4</td>
<td>97.5</td>
<td>0.456</td>
<td>0.568</td>
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<tr>
<td></td>
<td>3.74</td>
<td>16.94</td>
<td>95.3</td>
<td>96.5</td>
<td>1.72</td>
<td>0.610</td>
</tr>
<tr>
<td></td>
<td>9.68</td>
<td>12.53</td>
<td>90.9</td>
<td>93.5</td>
<td>2.55</td>
<td>0.722</td>
</tr>
<tr>
<td></td>
<td>14.81</td>
<td>9.41</td>
<td>83.3</td>
<td>—</td>
<td>3.55</td>
<td>1.01</td>
</tr>
</tbody>
</table>

\* The reaction time is corrected for the change of volume of the reaction system during the time course of the reaction. See ref. (5).
decomposition were evaluated from the results of the ammonia decomposition and the accompanying nitrogen exchange of $^{15}$N between ammonia and nitrogen gas as follows. The net rate of decomposition is given as

$$\frac{dP_A}{dt} = V_+ - V_-,$$

where $P_A$ the partial pressure of ammonia and $t$ the reaction time. The rate of decrease of $^{15}$N-enriched ammonia is given as

$$\frac{1}{2} \frac{d(P_AZ_A)}{dt} = Z_A V_+ - Z_N V_-,$$

where $Z^A$ or $Z^N$ is the respective atomic fraction of $^{15}$N in ammonia or nitrogen gas. Solving the above equations and $Z_A P_A + 2Z_N P_N = \text{const.}$ with respect to $V_+$ and $V_-$, we have

$$V_+ = -\frac{P_N}{Z^A - Z^N} \frac{dZ^N}{dt}$$

and

$$V_- = -\frac{1}{2} \frac{P_A}{Z^A - Z^N} \frac{dZ^A}{dt},$$

where $P_N$ is the partial pressure of nitrogen. Figure 1 shows the logarithmic plots of $V_+$ and $V_-$ against $P_A$\footnote{It is difficult to obtain graphically the value of the factor, $\frac{dZ^N}{dt}$, in Eq. (3.1). Therefore $V_+$ was evaluated by substituting $V_-$ into Eq. (1) instead of using Eq. (3.1). The $V_-$ was evaluated by Eq. (3.2).}. They are found to be nearly proportional to $P_A$ and $1/P_A$, respectively, for every catalyst except the No. 4 catalyst.

The $\nu_r$-value is defined as\footnote{where $\frac{-\Delta F}{RT} \ln V_+ / V_-$ has the usual meaning. The partial pressures of nitrogen and hydrogen were almost kept constant during the time course of the reaction, hence Eq. (4) is approximated as $\log V_+ / V_- = 2/\nu_r \log P_A + \text{const.}$}

$$\nu_r = \frac{-\Delta F}{RT \ln V_+/V_-},$$

Figure 2 shows this relation, from which the $\nu_r$-value were estimated at nearly unity for every catalyst. This result is in agreement with those observed by Tanaka et al.\footnote{or one of the present authors and Tanaka\footnote{The $V_-$ was evaluated by Eq. (3.2).}} over the singly- or doubly-promoted iron catalysts, respectively.

A. Kazusaka and I. Toyoshima
In connection with the mechanism of ammonia decomposition, it is interesting to compare the rate of nitrogen isotope equilibration reaction, $^{15}N_2 + ^{15}N_2 = 2^{15}N_2$, with that of ammonia decomposition. The formation rate of $^{15}N_2$ or $^{15}N_2$ is given as

$$\frac{d(PZ_N)}{dt} = 2Z_N^{(s)}(1-Z_N^{(s)})v_+ - Z_N^{(s)}v_- \quad (5.1)$$
or

\[
\frac{d(P_N Z^N)}{dt} = \{Z^{N(a)}\}^2 v_+ - Z^N v_-, \tag{5.2}
\]

where \( v_+ \) or \( v_- \) is the desorption or adsorption rate of nitrogen, \( Z^1 \) or \( Z^2 \) the mole fraction of \( ^{29}\text{N}_2 \) or \( ^{30}\text{N}_2 \) in nitrogen gas and \( Z^{N(a)} \) the atomic fraction of \( ^{15}\text{N} \) in the adsorbed nitrogen, respectively. Solving Eq. (5), \( \frac{dP_N}{dt} = v_+ - v_- \) and \( Z^A P_A + 2 Z^N P_N = \text{const.} \) with respect to \( v_+ \), \( v_- \) and \( Z^{N(a)} \), where \( Z^N = 1/2 Z^1 + Z^2 \), we have

\[
v_+ = \frac{P_N}{Z^{N(a)} - Z^N} \frac{dZ^N}{dt}, \tag{6.1}
\]

\[
v_- = \frac{1}{Z^{N(a)} - Z^N} \left[ -\frac{1}{2} P_A \frac{dZ^A}{dt} - \frac{1}{2} (Z^A - Z^{N(a)}) \frac{dP_A}{dt} \right] \tag{6.2}
\]

and

\[
Z^{N(a)} = \frac{\frac{dZ^N}{dZ^A}}{\frac{dZ^N}{dZ^1}} \pm \sqrt{\left(\frac{dZ^N}{dZ^1}\right)^2 - \left\{ 1 + 2 \left(\frac{dZ^N}{dZ^1}\right) \left(\frac{dZ^N}{dZ^1}\right) - Z^2 \right\}} \tag{6.3}
\]

From Eq. (3) and (6), we have

\[
\frac{v_+}{V^+} = \frac{Z^A - Z^N}{Z^{N(a)} - Z^N} \tag{7.1}
\]

and
The evaluated values of $Z^{(a)}$ is found to be nearly equal to $Z^A$ as shown in Table 2. The ratios of $v_+ / V_+$ and $v_- / V_-$ are thus close to unity, that is, each unidirectional rate of ammonia decomposition is equal to that of nitrogen equilibration reaction for every catalyst. This result gives the conclusion that both the reactions are rate-determined by the same step.

In the previous paper [6] we found that the rate expression of ammonia decomposition changed from $k(P_A/P_{H^5})$ to $k'(P_A/P_{H^2})$ by the increase of the amount of potassium oxide promoter, where $k$, $k'$, $\alpha$ and $\beta$ are the constants and $P_H$ is the partial pressure of hydrogen. These results were explained to be caused by the change of the rate-determining step from the step (8.2) to the step (8.5) of the following reaction scheme:

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_2(a) + \text{H}(a), \quad 2 \\
\text{NH}_2(a) & \rightarrow \text{NH}(a) + \text{H}(a), \quad 2 \\
\text{NH}(a) & \rightarrow \text{N}(a) + \text{H}(a), \quad 2 \\
2\text{H}(a) & \rightarrow \text{H}_2, \quad 3 \\
2\text{N}(a) & \rightarrow \text{N}_2. \quad 1
\end{align*}
\]

The number annexed to each steps is the stoichiometric number. According to the above explanation the $v_r$-value must change from two to unity by increasing the content of $K_2O$. This is not agreeable to the observed results of the $v_r$-value in the present investigation.

We further found that the rate of nitrogen isotope equilibration reaction was affected by the presence of hydrogen over the No. 1 catalyst but not over the No. 2, No. 3 and No. 4 catalysts [6]. On the basis of these findings it was concluded that the surface of the No. 1 catalyst might be covered by hydrogenated nitrogen, whereas the surface of the No. 2, No. 3 or No. 4 catalyst might be covered by adsorbed nitrogen, that is, the mechanism proposed by Temkin and Pyzhev [12] was valid in the case of the No. 2, No. 3 and or No. 4 catalyst, but not over No. 1 catalyst.

Consequently, the scheme (8) with the rate-determining step (8.5) is agreeable to the result obtained over the No. 2, No. 3 or No. 4 catalyst, but not that obtained over the No. 1 in the present experimental conditions.

The amount of potassium oxide promoter thus affects severely the reaction mechanism of ammonia decomposition, changing the adsorbed species on the catalyst surface. This conclusion is in conformity with that of the previous kinetic study [6].
A. Kazusaka and I. Toyoshima

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