Study on the Reduction Process of Vanadium Oxide Catalysts by Means of Infrared Spectroscopy and X-ray Diffraction

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Study on the Reduction Process of Vanadium Oxide Catalysts by Means of Infrared Spectroscopy and X-ray Diffraction

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By x-ray diffraction and infrared spectroscopy, the changes of the structures of V2O5, V2O5-25% MoO3 and V2O5-7% WO3, respectively, were investigated in the course of reduction with cyclohexane or NH3. V2O5-catalysts were reduced to V2O4 via V2O5+V2O4 and V12O26 under the mild conditions. The doping MoO3 or WO3 into V2O5 in the range of the formation of the solid solution caused the increase in the reducibility of the catalyst and in the stability of the crystal structure of V2O5, simultaneously.

INTRODUCTION

The reduction process of vanadium (V) oxide (V2O5) has been already studied by a number of researchers. In the previous work, it was observed that V2O5 was directly reduced to V2O5 with H2 at temperatures above 500°C, but reduced to V2O5 via V7O5+6 with SO2 or NH3, and the V2O5-MoO3 was more easily reduced than V2O5 with C6H6 at temperatures below 300°C. Simard et al. investigated the composition of V2O5 catalyst during oxidation of o-xylene and recognized that the composition of catalyst as a function of catalyst bed depth varied to V12O26, V2O5 and V2O3. Matsuura observed microscopically the color change of V2O5 crystal in the course of reduction with H2, and clarified that after the surface was covered with reduced layer of V2O5, reduction into the bulk phase of the crystal proceeded. Recently, such new compounds as V3O7, V4O9 and two kinds of V12O268 were found in the reduction process of V2O5 by means of x-ray diffraction.

In the present work, x-ray diffraction and infrared spectroscopy were adopted to elucidate the changes of the crystal structure and of the state of the V=O bond of powdered V2O5, V2O5-25% MoO3 and V2O5-7% WO3, respectively, in the course of reduction with cyclohexane (C6H12) or NH3 under relatively mild conditions.

EXPERIMENTAL

1. Materials

a) V2O5-sample was prepared by the calcination of NH4VO3 (extrapure grade) at 450°C for 6 hr in dry air stream.

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b) Sample of V₂O₅-25% MoO₃ was prepared as follows. V₂O₅ given above and MoO₃, which was obtained from chemical pure grade (NH₄)₂Mo₇O₂₇ in the same way as V₂O₅, were mixed in the molar ratio of 3:1, melted together at 700°C for 30 min in a quartz crucible, allowed to cool in the furnace, and the solidified sample was ground to powder of about 200 meshes.

c) Sample of V₂O₅-7% WO₃ was prepared in the similar way as V₂O₅-MoO₃ sample. WO₃ was obtained from chemical pure grade (NH₄)₁₀W₁₂O₄₁·5H₂O.

d) C₆H₁₂ (extrapure grade cyclohexane) which was dried over metallic Na was further purified by distillation.

e) NH₃-gas from commercial cylinder was dried over anhydrous silica gel before use.

2. Apparatus and Procedure

a) Reduction with C₆H₁₂. The catalyst-samples (300-500 mg) were charged with 30 cc of liquid C₆H₁₂ in an autoclave and were treated in the range of temperatures of 80°C to 400°C for 5 hr in the N₂ atmosphere.

b) Reduction with NH₃. The samples were reduced in a stream of NH₃ gas in a pyrex glass tube heated at 300°C-400°C. The conditions of reduction are summarized in Table 1.

Table 1. The conditions of reduction.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Duration</th>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Duration</th>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-C-1</td>
<td>102</td>
<td>5 hr</td>
<td>M-C-1</td>
<td>80</td>
<td>5 hr</td>
<td>W-C-1</td>
<td>150</td>
<td>5 hr</td>
</tr>
<tr>
<td>V-C-2</td>
<td>130</td>
<td>&quot;</td>
<td>M-C-2</td>
<td>100</td>
<td>&quot;</td>
<td>W-C-2</td>
<td>200</td>
<td>&quot;</td>
</tr>
<tr>
<td>V-C-3</td>
<td>176</td>
<td>&quot;</td>
<td>M-C-3</td>
<td>144</td>
<td>&quot;</td>
<td>W-C-3</td>
<td>250</td>
<td>&quot;</td>
</tr>
<tr>
<td>V-C-4</td>
<td>204</td>
<td>&quot;</td>
<td>M-C-4</td>
<td>220</td>
<td>&quot;</td>
<td>W-C-4</td>
<td>300</td>
<td>&quot;</td>
</tr>
<tr>
<td>V-C-5</td>
<td>262</td>
<td>&quot;</td>
<td>M-C-5</td>
<td>280</td>
<td>&quot;</td>
<td>W-C-5</td>
<td>400</td>
<td>&quot;</td>
</tr>
<tr>
<td>M-C-6</td>
<td>300</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-C-7</td>
<td>400</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V-N-1</td>
<td>300</td>
<td>10 min</td>
<td>M-N-1</td>
<td>350</td>
<td>15 min</td>
<td>W-N-1</td>
<td>350</td>
<td>15 min</td>
</tr>
<tr>
<td>V-N-2</td>
<td>350</td>
<td>15 min</td>
<td>M-N-2</td>
<td>&quot;</td>
<td>1 hr</td>
<td>W-N-2</td>
<td>&quot;</td>
<td>1 hr</td>
</tr>
<tr>
<td>V-N-3</td>
<td>&quot;</td>
<td>1 hr</td>
<td>M-N-3</td>
<td>400</td>
<td>&quot;</td>
<td>W-N-3</td>
<td>400</td>
<td>&quot;</td>
</tr>
<tr>
<td>V-N-4</td>
<td>400</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All C series samples were reduced with cyclohexane.
All N series samples were reduced with ammonia.

c) X-ray diffraction. A diffractometer of GX-111B type by the Shimadzu Co. Ltd. was used. Measurements were carried out at room temperature using Cu-target.

d) Infrared spectroscopy. A Shimadzu IR-27 type spectrometer was used. Absorption spectra for the samples suspended in Nujol were recorded in the range of wave number of 600 cm⁻¹ to 1200 cm⁻¹, by using NaCl-cell.
EXPERIMENTAL RESULTS

1. Colour Change of Catalyst in the Course of Reduction

$V_2O_5$-sample was initially orange yellow, but in proceeding of reduction with $C_6H_{12}$ or $NH_3$, its colour changed to dark blue through brown. Such the colour change in the course of reduction is expectable from the previous observation by chemical and x-ray analyses that $V_2O_5$ (orange yellow) was reduced to $V_2O_4$ (blue black) via $V_2O_2$ (dark blue) with $SO_2$ or $NH_3$ at temperatures below 400°C.\(^1\)

$V_2O_5$-MoO$_3$ sample was initially green, because this contained about 6\% of $V^{4+}$ and its colour changed to dark blue through dark green by reduction. In the case of $V_2O_5$-WO$_3$ sample which contained about 2\% of $V^{4+}$, its colour changed from brown to dark blue.

2. X-ray Diffraction

a) $V_2O_5$: The x-ray diffraction patterns of the samples reduced with $C_6H_{12}$ ($V$-$C$ series) are shown in Fig. 1. No structural change from $V_2O_5$ was observed.
Table 2. The changes of the crystal structures.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>V_{2}O_{5}</th>
<th>V_{2}O_{5}-25% MoO_{3}</th>
<th>V_{2}O_{5}-7% WO_{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-</td>
<td>V_{2}O_{5}</td>
<td>M-C-1 V_{2}O_{5}</td>
<td>W-C-1 V_{3}O_{5}</td>
</tr>
<tr>
<td>200-</td>
<td>V_{2}O_{5}</td>
<td>M-C-2 V_{2}O_{5}</td>
<td>W-C-1 V_{3}O_{5}</td>
</tr>
<tr>
<td></td>
<td>V-C-3 V_{2}O_{5}+V_{4}O_{4} (t)</td>
<td>M-C-3 V_{2}O_{5}</td>
<td>W-C-1 V_{3}O_{5}</td>
</tr>
<tr>
<td></td>
<td>V-C-4 V_{2}O_{5}+V_{4}O_{4} (s)</td>
<td>M-C-4 V_{2}O_{5}</td>
<td>W-C-3 V_{2}O_{4}+V_{2}O_{4} (t)</td>
</tr>
<tr>
<td></td>
<td>V-C-5 V_{12}O_{26}</td>
<td>M-C-5 V_{2}O_{5}+V_{2}O_{4} (s)</td>
<td>W-C-3 V_{2}O_{4}+V_{2}O_{4} (t)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M-C-6 V_{2}O_{5}+V_{4}O_{4} (s) +V_{12}O_{26} (t)</td>
<td>W-C-4 V_{2}O_{5}+V_{12}O_{26} (s)</td>
</tr>
<tr>
<td>300-</td>
<td></td>
<td>M-C-7 V_{2}O_{5}+ (?)</td>
<td>W-C-5 V_{12}O_{26}+ (?)</td>
</tr>
<tr>
<td>400-</td>
<td>V-N-1 V_{2}O_{5}+V_{4}O_{4} (s)</td>
<td>M-N-1 V_{2}O_{5}+V_{4}O_{4} (t)</td>
<td>W-N-1 V_{2}O_{5}+V_{4}O_{4} (t)</td>
</tr>
<tr>
<td>350-</td>
<td>V-N-2 V_{2}O_{5}+V_{4}O_{4}</td>
<td>M-N-2 V_{2}O_{5}+V_{4}O_{4} (t)</td>
<td>W-N-2 V_{2}O_{5}+V_{4}O_{4} +V_{12}O_{26} (s)</td>
</tr>
<tr>
<td></td>
<td>V-N-3 V_{12}O_{26}</td>
<td>M-N-3 V_{12}O_{26}+V_{4}O_{4}</td>
<td>W-N-3 V_{12}O_{26}+V_{4}O_{4} (s)</td>
</tr>
<tr>
<td></td>
<td>V-N-4 V_{2}O_{4}+V_{12}O_{26}</td>
<td>s: small amount</td>
<td>t: trace</td>
</tr>
</tbody>
</table>

Fig. 2. X-ray diffraction patterns of V-N series.
for V-C-1 and V-C-2 which were treated at temperatures below 130°C. In the case of V-C-3 and V-C-4, weak diffraction lines at d=3.20, 2.13 and 1.65 (2θ=27.8, 42.4 and 55.7) appeared additionally. These lines correspond to the three strong lines of V₂O₅. V-C-5 reduced at 262°C showed a remarkably different pattern from those of V₂O₅ and V₂O₄. This pattern corresponds completely with that of the compound which was identified as V₁₂O₃₀ previously. The x-ray diffraction patterns of samples reduced with NH₃ (V-N series) are shown in Fig. 2. The patterns of V-N-1 and V-N-2, which were reduced at temperatures below 350°C for 15 min, were mainly composed of that of V₂O₅ and contained additionally some diffraction lines corresponding to that of V₂O₄. The pattern of V-N-3 reduced at 350°C for 1 hr was similar to that of V₁₂O₃₀ observed in V-C-5. In the case of V-N-4 reduced at 400°C, the four strong lines of V₂O₅ (2θ=27.9, 37.2, 42.1 and 55.5) were observed besides that of V₁₂O₃₀.

These results show that the crystal structure of V₂O₅-samples varies with reduction under the relatively mild condition as listed in Table 2 (column A).

b) V₂O₅-MoO₃: Figure 3 shows the diffraction patterns of the samples reduced
with C₆H₁₂ (M-C series). The V₂O₅·25% MoO₃ gave the similar diffraction pattern to that of V₂O₅ as reported previously. This fact shows that the sample is a solid solution of V₂O₅ and MoO₃, and has almost same crystal structure as that of V₂O₅. No structural change was observed in the sample M-C-1 to M-C-4 which were reduced at temperatures below 220°C. In the diffraction pattern of M-C-5 reduced at 280°C, a strong line at 2θ=27.7 and a very weak line at 2θ=37.3 could be observed. This means the structure of this sample changed partially to the similar one to that of V₂O₄. The M-C-6 sample reduced at 300°C gave the diffraction pattern which composed of somewhat stronger lines of V₂O₄-structure than that of M-C-5 and of additional weak lines corresponding to V₁₅O₄₆-structure (2θ=25.0 and 33.7). But even in the cases of both samples of M-C-5 and M-C-6, the main crystal structure was similar to that of V₂O₅. M-C-7 reduced at 400°C gave a remarkably different pattern, some lines of which could be ascribed to that of V₂O₃-structure (2θ=24.5, 33.0 and 36.2) but another lines could not be yet assigned.

As shown in Fig. 4, the pattern of M-N-2 which were reduced with NH₃ at 350°C were mainly composed of similar one to that of V₂O₅, but the former con-
Study on Reduction Process of Vanadium Oxide Catalysts

tained an additional weak line (2θ=28.0) probably belonging to V₂O₅-structure, while the latter contained weak lines belonging to V₁₂O₃₆⁻ and V₃O₆⁻ structures. In the pattern of M-N-3 reduced at 400°C, the diffraction lines of V₁₂O₃₆⁻ and V₃O₆⁻ structures were observed with about equal intensity.

In Table 2 (column B), the changes of the crystal phases in the reduction process of V₂O₅-MoO₃ catalysts are summarized.

c) V₂O₅-WO₃: The x-ray diffraction patterns of samples of W-C series are shown in Fig. 5. The starting sample which contained 7 mol % of WO₃ gave the characteristic x-ray diffraction pattern of V₂O₅-structure as in the case of V₂O₅-MoO₃ samples. W-C-1 and W-C-2 samples which were reduced at temperatures below 200°C, did not show any structural change from the starting sample. In the diffraction pattern of W-C-3 sample reduced at 250°C, a line corresponding to the strongest line of V₂O₅ appeared additionally. The diffraction pattern of W-C-4 sample reduced at 300°C was composed of the pattern of V₁₂O₃₆⁻-structure (2θ=14.3, 25.3, 30.3, 33.6, 43.8 and 45.0) and that of V₃O₆⁻-structure. A remarkably
different pattern was observed for W-C-5 sample reduced at 400°C. In this pattern, diffraction lines corresponding to those of V₁₂O₃₅-structure were observed besides two strong lines (2θ=45.0 and 46.5) which could not be yet assigned.

The diffraction patterns of W-N series samples are shown in Fig. 4. W-N-1 sample which was reduced at 350°C for 15 min, almost retained the V₂O₅-structure with very small portion of V₂O₄-structure. The structure of W-N-2 reduced at 350°C for 1 hr was mainly V₂O₄-structure and partially V₂O₅- and V₁₂O₃₅-structure. The pattern of W-N-3 mainly composed of diffraction lines of V₁₂O₃₅-structure besides weak lines of V₂O₄-structure. In Table 2 (column C), the changes of the crystal phases of W-C and W-N series samples are summarized.

3. Infrared Spectra

a) V₂O₅: The infrared spectrum of V₂O₅ has two characteristic absorption bands at 1025 cm⁻¹ and 830 cm⁻¹. The former band is relatively sharp one due to the stretching vibration of the (V=O)³⁺ bond and the latter band is broad one arised probably from the V-O-V bond.¹³

Figure 6 shows the infrared spectra of the samples of V-C series. In this figure, it is apparently observed that the characteristic band of the V=O bond was retained in the samples which were reduced with C₆H₁₂ at temperatures below 204°C, but in the spectrum of M-C-7, this band diminished. (An absorption band

![Infrared absorption spectra of V-C series.](image-url)
The infrared spectra of samples of V-N series are shown in Fig. 7, and the spectra of V-N-1 and V-N-2 retained the V=O bond, but in the cases of V-N-3 and V-N-4, no V=O bond was observed.

\[ V_2O_5 \]
\[ V-N-1 \]
\[ V-N-2 \]
\[ V-N-3 \]
\[ V-N-4 \]

**Fig. 7. Infrared absorption spectra of V-N series.**

(b) \( V_2O_5-MoO_3 \): The infrared spectrum of this sample was similar to that of \( V_2O_3 \), but the absorption peak at 1025 cm\(^{-1} \) shifted to a longer wave length and became broader as the results of increase of \( V^{4+} \) ions.\(^{12} \) Figure 8 shows infrared spectra of M-C series. The characteristic band due to the V=O bond was observed in the spectra of the samples from M-C-1 to M-C-5 and in the infrared spectra of M-C-4 and M-C-5, absorption A appeared. Furthermore, in the case of M-C-6, another new broad band at 920 cm\(^{-1} \) (absorption B in Fig. 8) was observed. This broad band is probably associated with \( V_{12}O_{25} \)-structure in comparison with the result of x-ray analysis. The infrared spectrum of M-N-1 composed of characteristic band due to the V=O bond and absorption A, but M-N-2 and M-N-3 did not show any clear absorption band (Fig. 9).

c) \( V_2O_5-WO_3 \): As shown in Fig. 9 and 10, the infrared spectra of \( V_2O_5-WO_3 \) changed by reduction in a similar manner as \( V_2O_5-MoO_3 \). But in this case, the V=O bond diminished by milder reduction than in the case of \( V_2O_5-MoO_3 \) samples. In the spectra of W-C-3, W-C-4 and W-N-1, the absorption A and/or absorption B
could be observed.

Fig. 8. Infrared absorption spectra of M-C series.

Fig. 9. Infrared absorption spectra of M-N and W-N series.
DISCUSSION

From the results of x-ray diffraction, it was found that V$_2$O$_5$ were partially formed in advance of V$_{12}$O$_{26}$, which is more oxidised state than V$_2$O$_5$, in the course of reduction of vanadium oxide catalysts.

The results mentioned above can be understood by remembering small diffusion constants of oxygen ions in these catalysts. The present authors studied previously the reduction rates of V$_2$O$_5$ and V$_2$O$_5$:MoO$_3$ (MoO$_3$ : 24.1 mol%) catalysts with H$_2$ or benzene and found that V$_2$O$_5$:MoO$_3$ was more reducible than V$_2$O$_5$, and that the rate determining step of the reduction was the diffusion process of oxygen ions in the crystal.$^{5,6,7}$ The obtained values of apparent diffusion constants had been

$$D_{V_2O_5} = 3.84 \times 10^4 \exp \left( -20100/RT \right)$$
$$D_{V_2O_5:MoO_3} = 7.06 \times 10^5 \exp \left( -12800/RT \right)$$

for V$_2$O$_5$ and V$_2$O$_5$:MoO$_3$ catalyst respectively.

These equations reveal also that V$_2$O$_5$:MoO$_3$ catalyst is more reducible than V$_2$O$_5$ catalyst at temperatures below 300°C.

Now, the formation of V$_2$O$_5$ in advance of V$_{12}$O$_{26}$ suggests that the diffusion
rate of oxygen ions in the crystal is not so rapid enough to cause homogeneous reduction through the whole crystal-phase, thus $V_2O_5$ is partially formed on the surface even though bulk phase of the crystal retains the crystal structure of $V_2O_5$.

It is interesting that though $V_2O_5$-$MoO_3$ catalyst is more reducible than $V_2O_5$ catalyst under this experimental condition, the $V_2O_5$-structure is retained until more higher reduction temperature than in the case of $V_2O_5$, and that $V_2O_4$-structure which is formed in advance of $V_2O_6$ does not grow large. This can be explained by noticing the difference in diffusion constants of these samples. In the $V_2O_5$-$MoO_3$ catalysts, the diffusion of oxygen ions is easier than in $V_2O_5$ catalyst, thus oxygen ions may be furnished to the surface layer from inner part of crystal to prevent heterogeneous local reduction of surface layer.

There is no available value of the apparent diffusion constant for $V_2O_5$-$WO_3$ catalyst. However, the rate of the diffusion of oxygen ions has a correlation with the concentration of oxygen vacancy (or $V^{4+}$ ions), and the concentration of $V^{4+}$ varies in order of $V_2O_5$-$V_2O_5$-$WO_3$-$V_2O_5$-$MoO_3$. Therefore, the reducibility and mobility of oxygen ions in this catalyst are assumed to be intermediate between $V_2O_5$-$MoO_3$ and $V_2O_5$. This assumption explains the results of x-ray diffraction measurements of $V_2O_5$-$WO_3$ catalyst.

The above explanation for the doping effect of MoO$_3$ or WO$_3$ is supported by the results of infrared spectroscopic measurements, too. The characteristic band due to $V=O$ bond shifted to a longer wave length and grew broader by doping MoO$_3$ into $V_2O_5$. This fact means that the $V=O$ bond of the $V_2O_5$-$MoO_3$ catalyst become more reactive than that of the $V_2O_5$ catalyst, and that as the result of this effect, the reducibility of the catalyst increases. The critical reduction conditions under which the characteristic $V=O$ bond of the $V_2O_5$-structure is retained or not in the catalyst, are summarized in Table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>By reduction with $C_6H_{12}$</th>
<th>By reduction with $NH_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2O_5$</td>
<td>at 204°C $\bigcirc$</td>
<td>at 350°C for 15 min $\triangle$</td>
</tr>
<tr>
<td></td>
<td>at 282°C $\times$</td>
<td>at 350°C for 1 hr $\times$</td>
</tr>
<tr>
<td>$V_2O_5$-$MoO_3$</td>
<td>at 280°C $\bigcirc$</td>
<td>at 350°C for 15 min $\triangle$</td>
</tr>
<tr>
<td></td>
<td>at 300°C $\times$</td>
<td>at 350°C for 1 hr $\times$</td>
</tr>
<tr>
<td>$V_2O_5$-$WO_3$</td>
<td>at 250°C $\triangle$</td>
<td>at 350°C for 15 min $\triangle$</td>
</tr>
<tr>
<td></td>
<td>at 300°C $\times$</td>
<td>at 350°C for 1 hr $\times$</td>
</tr>
</tbody>
</table>

$\bigcirc$ means that the absorption band by $V=O$ bond could be observed clearly.
$\triangle$ means that the weak absorption band by $V=O$ bond could be observed.
$\times$ means that the absorption band by $V=O$ bond could not be observed.

Table 3 reveals that the $V=O$ bond is retained up to higher reduction temperature in order of $V_2O_5$-$V_2O_5$-$WO_3$-$V_2O_5$-$MoO_3$ at temperatures below 300°C. As the $V=O$ bond is associated with the characteristic crystal structure of $V_2O_5$, the retention of this bond reflects probably the stability of $V_2O_5$-structure.

It is noteworthy that in the $V_2O_5$-$MoO_3$ and $V_2O_5$-$WO_3$ catalysts, the samples,
which still had a crystal phase of V$_2$O$_5$, did not show the absorption band due to V=O bond (M-C-6 and W-C-4). This fact can be explained, if the infrared spectra reflected mainly the state of the thin surface layer of the samples. In the case of the V$_2$O$_5$ catalyst, the reduction proceeds heterogeneously in the surface and V$_2$O$_4$ is formed locally. Therefore, the V=O bond associated with V$_2$O$_5$-structure remains in the surface. On the other hand, in the case of V$_2$O$_5$-MoO$_3$ and V$_2$O$_5$-WO$_3$ catalysts, reduction proceeds homogeneously in the surface as mentioned above, so the V=O bond may diminish in the surface layer even if the V$_2$O$_5$-structure remains in the bulk phase.

In conclusion, the V$_2$O$_5$-catalyst are reduced to V$_2$O$_4$ via V$_2$O$_4$+V$_2$O$_5$ and V$_{12}$O$_{26}$ from the surface layer under the mild condition and by doping MoO$_3$ or WO$_3$ into V$_2$O$_5$ in the range of formation of solid solution, the crystal structure of V$_2$O$_5$ become more stable in spite of increase in its reducibility. It is presumed that this effect of MoO$_3$ or WO$_3$ correlates closely with its promotive action on V$_2$O$_5$-catalyst in oxidation reaction.

**REFERENCES**