# OXIDATION OF CYCLOPENTADIENE OVER VANADIUM OXIDE AND ITS MIXED OXIDES

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**Abstract**—Oxidation of cyclopentadiene over vanadium oxide and its mixed oxides has been studied and correlated to changes of vanadium valence. There are various organic products containing one or two oxygen atoms besides maleic anhydride. The catalyst V-Ag-O shows the highest selectivity to maleic anhydride. The results indicate that the reaction follows the redox mechanism. The additives are thought to moderate the tendency of an oxide to donate its oxygen.

## INTRODUCTION

It will be very valuable to develop the use of $C_5$-fractions for chemical raw material, in view of resources conservation. Partial oxidation by air may be a cheap way to use $C_5$-fractions. In the case of cyclopentadiene(CPD), which is one of its major components, there are some reports [1-5] that it can be oxidized to maleic anhydride(MA) selectively, its selectivity being comparable to benzene. As selective catalysts, V-Mo-O, V-Ag-O and V-Mo-P-O were reported.

However, there has been few systematic study on catalyst and reaction mechanism. The aim of this study is to understand the effects of catalyst components on catalytic behavior in connection with reaction mechanism for oxidation of CPD. In this work V-O, V-P-O, V-Mo-O, V-Mo-P-O and V-Ag-O supported on $\alpha$-alumina were studied and compared.

## EXPERIMENTAL

### Catalyst preparation

Five catalysts were prepared referring to literatures [1-3, 5-7] on oxidation of hydrocarbons to MA. $\alpha$-Alumina powder was added to aqueous solution of active component(s) and the slurry was evaporated to paste. The amount of $\alpha$-alumina was 5 wt/wt of active component(s). The paste was dried at 120°C for 10 hrs and crushed. After sieving, the particles of 1-2 mm size were calcined at 500°C for 3 hrs.

As the sources of active components, ammonium vanadate, ammonium biphosphate, ammonium molyb-

date and silver nitrate were used. For the dissolution of ammonium vanadate, excess oxalic acid was added as reducing agent. Surface areas of catalysts were determined by the BET method. The compositions and surface areas of catalysts are shown in Table 1.

### Apparatus and Methods

The reaction apparatus is shown in Fig. 1. Feed stream was obtained by continuous injection of dicyclopentadiene into air stream using syringe pump and cracking to monomer at 300°C in mixing chamber. The purity of CPD in feed stream was higher than 99% and its impurities were dicyclopentadiene and benzene. The flow rate of feed stream was 5.56 cc/sec ($2.48 \times 10^{-4}$ mole/sec) and the concentration of CPD was 0.6 mole%. The reactor was made of a Pyrex tube of 1.4 cm i.d. and 26 cm length. A movable thermocouple was mounted along the axis of the reactor to measure the temperature. The catalysts were diluted with quartz particles and placed between zones of quartz particles.

For selectivity comparison, maximum selectivity to

**Table 1. The composition and surface area of prepared catalyst.**

| Cat. No. | Active component (atom ratio) | Surface area $(m^2/g)$ |
|---|---|---|
| 1 | V | 1.6 |
| 2 | V:P (1:1) | 1.7 |
| 3 | V:Mo (1:0.2) | 1.3 |
| 4 | V:Mo:P (1:0.2:0.02) | 1.5 |
| 5 | V:Ag (1:0.003) | 1.0 |

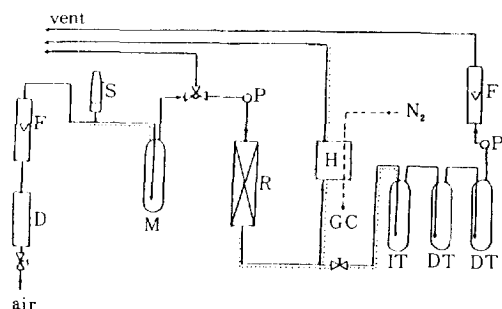\* To whom all correspondence should be addressed.

**Fig. 1. Schematic diagram of reaction apparatus:**
D, drying tube; F, flowmeter; S, syringe pump; M, mixing chamber; P, sampling port; R, reactor; H, heated gas sampler; IT, ice trap; DT, dry ice trap; ……, heating band.

MA was investigated over 4 cc of each catalyst (GHSV = 5000hr$^{-1}$), varying reaction temperature(300-490°C). For activity comparison, the consumption of CPD was investigated at 350°C, increasing catalyst amount within 55% conversion in which region the temperature of the catalyst bed could be controlled in the difference of ± 1°C.

The analysis of the inlet and outlet gases of the reactor was carried out by two gas chromatographs for determination of conversion and selectivities. CPD and organic products were analyzed by Shimadzu 8A-FID with 2m TENAX-GC column for which the temperature is programmed from 100°C to 300°C at a rate of 10°C min$^{-1}$. Inorganic products such as CO and $CO_2$ were analyzed by Shimadzu 8A-TCD with 3m Carbosieve-S and 2m Porapak-Q columns at 50°C. The organic products condensed in cold traps were identified by GC/MS and comparison of retention time with standard sample.

**Analysis of vanadium valence**

The changes of vanadium valence in catalysts were investigated after the treatment shown in Table 2. The amounts of $V^{5+}$, $V^{4+}$ and $V^{3+}$ were determined by manganometrical titration [8] after the sample was dissolved in 10% $H_2SO_4$ and fitered to remove α-alumina.

**Table 2. Conditions of reaction and reduction treatments.**

| Treatment | Reaction | Reduction |
|---|---|---|
| Amount of Cat. | 2 g | 1 g |
| Feed stream | CPD in Air (0.6%) | CPD in $N_2$ (0.6%) |
| Temperature | 350℃ | 350℃ |
| Time | 2 hrs | 5 mins |

## RESULTS

In this study, up to 20 organic products were determined besides MA by gas chromatography. Among these, identified compounds were acetaldehyde, furan, 2-cyclopenten-1-one, 4-cyclopentene-1,3-dione, 2H-pyran-2-one, 1-indanone and phthalic anhydride(PA). The rest could not be identified because of low concentrations.

The selectivity comparison of catalysts is shown in Table 3. For all catalysts, maximum selectivities to MA were reached at 100% conversion when organic by-product was only PA. Production of MA was highest over V-Ag-O and lowest over V-P-O which is a highly selective catalyst for butene to MA.

The results of CPD consumption at 350°C were plotted in Figs. 2-6. Product distribution does not change significantly despite increase of conversion under the condition of activity measurement. The average selectivity to each product for all catalysts is shown in Table 4.

**Table 3. The maximum selectivities to maleic anhydride over various catalysts.**

| Cat. No. | $S_{MA}$ (%) | $Y_{MA}$ (%) |
|---|---|---|
| 1 | 39.1 | 72.5 |
| 2 | 36.5 | 67.7 |
| 3 | 44.6 | 82.8 |
| 4 | 40.6 | 75.3 |
| 5 | 46.7 | 86.6 |



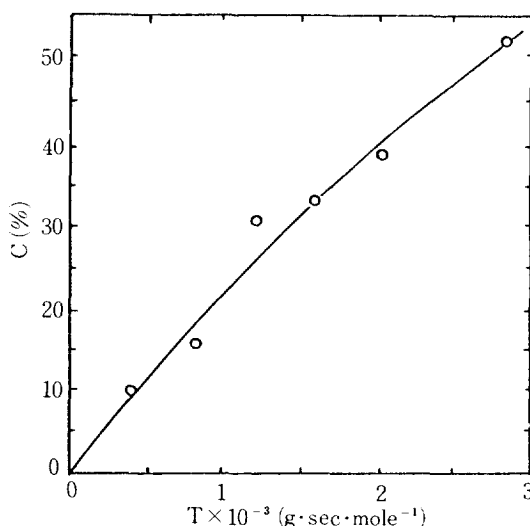**Fig. 2. Conversion vs. time factor for Cat. No. 1.**

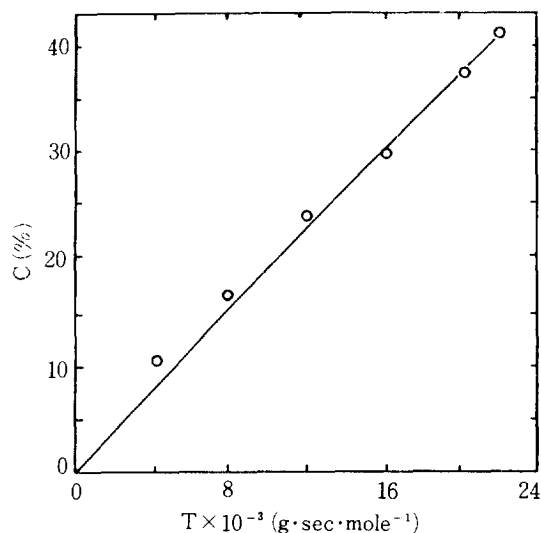Fig. 3.  Conversion vs. time factor for Cat. No. 2.



Fig. 5.  Conversion vs. time factor for Cat. No. 4.

In analysis of vanadium valence, amounts of $V^{3+}$ were small enough to be ignored for all catalysts. Reduction of $V^{5+}$ to $V^{4+}$ occured during reaction and reduction treatments. These results are shown in Table 5.

## DISCUSSION

In this experimental condition, oxygen partial pressure was so larger than cyclopentadiene that oxygen partial pressure remained virtually constant. Hence the rate of cyclopentadiene consumption is expressed as following.
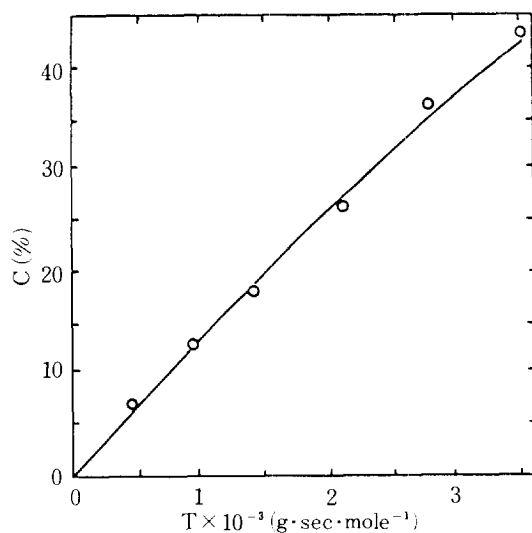
$$- r_c = -\frac{dP_c}{dT} = kP_c^n \qquad (1)$$

Since the change of gas molecules during reaction could be ignored as compared with total gas molecules, Eq. (1) becomes Eq. (2).

$$- r_c = -\frac{dF_c}{dT} = k' F_c^n \qquad (2)$$

Were, $F_c = 1 - \dfrac{C}{100}$

From the results of Figs. 2-6, empirical n and k' values were estimated according to integral method using a personal computer. The estimated results are shown in Table 6.
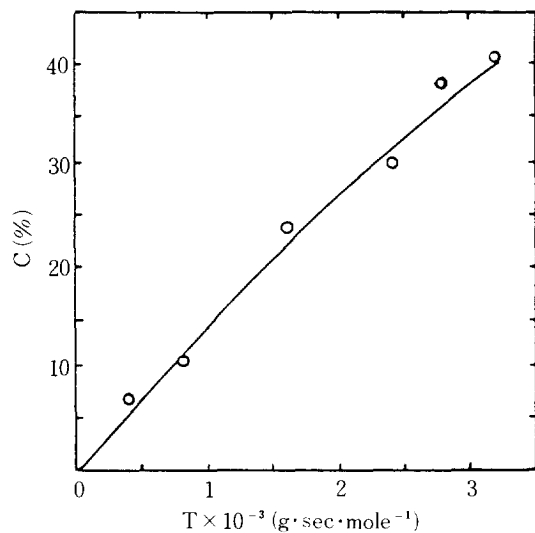


Fig. 4.  Conversion vs. time factor for Cat. No. 3.



Fig. 6.  Conversion vs. time factor for Cat. No. 5.

Table 4. Average selectivity to each product under the condition of activity measurement[a].

| Cat. No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $CO+CO_2$ | 35.3 | 32.3 | 32.0 | 32.0 | 32.6 |
| Acetaldehyde | 0.2 | 0.2 | 0.3 | 0.6 | 0.7 |
| Furan | 0.7 | 0.6 | 0.6 | 0.7 | 0.8 |
| Cyclopentenone | 5.6 | 10.0 | 8.2 | 8.6 | 6.5 |
| MA | 19.8 | 13.8 | 16.6 | 16.2 | 18.2 |
| Cyclopentendione | 10.4 | 9.5 | 8.6 | 8.4 | 10.2 |
| Pyranone | 4.4 | 4.3 | 5.3 | 5.9 | 4.9 |
| Indanone | 8.2 | 7.9 | 14.6 | 12.6 | 9.2 |
| PA | 2.1 | 1.8 | 1.9 | 2.2 | 1.9 |
| Others | 13.2 | 19.6 | 11.8 | 12.8 | 15.0 |

a. Temperature : 350℃, conversion ≦55%

In the case of butene to MA, redox mechanism [9] was occasionally applied to kinetic studies [10-12]. We will employ redox mechanism to interpret the oxidation of cyclopentadiene.

### i) Reaction order

According to redox mechanism, n of Eq. (2) must be greater than 0 and less than 1 [13]. If the potential rate of oxidation of the hydrocarbon by the catalyst exceeds that of the catalyst, n becomes 0. For the opposite case, n becomes 1. The more catalyst approaches to the former case, the larger-$\Delta$AV during reaction will be in Table 5. This relation accords with the experimental results as shown in Fig. 7.
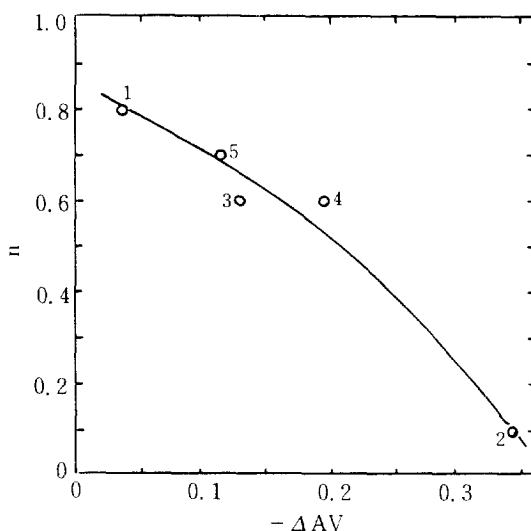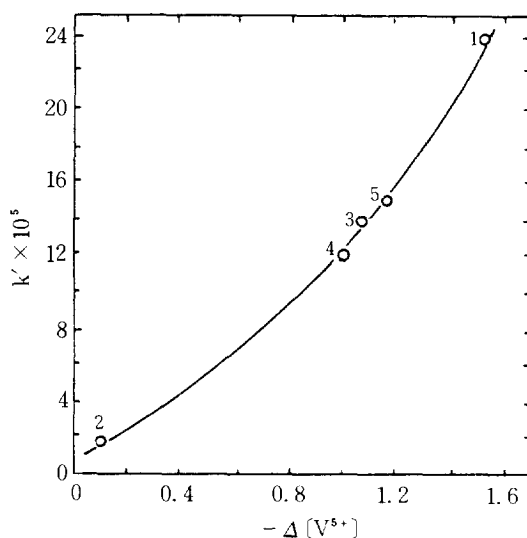
### ii) Activity

Based on redox mechanism, Sachtler and de Boer [14] postulated that activity and selectivity was

Table 5. Changes in average valence of vanadium and reduction rates of catalysts during treatments.

| Cat. No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| AV of fresh Cat. | 4.974 | 4.983 | 4.889 | 4.902 | 4.977 |
| $-\Delta$ AV during reaction | 0.035 | 0.345 | 0.128 | 0.196 | 0.113 |
| $-\Delta$ [$V^{5+}$] during reaction | 0.101 | 0.562 | 0.366 | 0.411 | 0.297 |
| $-\Delta$ AV during reduction | 0.545 | 0.050 | 0.498 | 0.451 | 0.390 |
| $-\Delta$ [$V^{5+}$] during reduction | 1.53 | 0.09 | 1.06 | 1.00 | 1.16 |

Table 6. Estimated kinetic parameters.

| Cat. No. | n | $k' \times 10^5$ |
|---|---|---|
| 1 | 0.8 | 24 |
| 2 | 0.1 | 1.9 |
| 3 | 0.6 | 14 |
| 4 | 0.6 | 12 |
| 5 | 0.7 | 15 |



Fig. 7. Relationship between n and $-\Delta$AV during reaction.



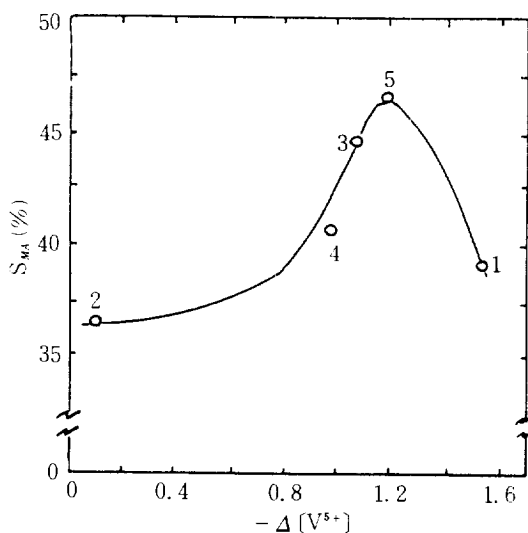Fig. 8. Relationship between k' and $-\Delta$ [$V^{5+}$] during reduction.

**Fig. 9. Relationship between maximum $S_{MA}$ and $-\Delta\,[V^{5+}]$ during reduction.**

dominated mainly by the tendency of an oxide to donate its oxygen.

Since the magnitude of $-\Delta[V^{5+}]$ during reduction can be considered as characteristic measure for the tendency of the catalyst to donate its oxygen, it will be proportional to catalyst activity. This is verified as shown in Fig. 3. The magnitudes of $-\Delta[V^{5+}]$ for mixed oxides are lower than vanadium oxide. It is thought that additives such as Ag, Mo and P play the role of moderating the tendency to donate oxygen.

**iii) Selectivity**

Selectivities also might be related to $-\Delta\,V^{5+}]$ during reduction. This is shown in Fig. 9. Maximum selectivity increases to Cat. No. 5 with $-\Delta[V^{5+}]$, and then decreases at Cat. No. 1. This could be explained in connection with product distribution under mild reaction condition. As shown in results, there are various products containing one or two oxygen atoms under mild condition which might be oxidized further to acid anhydrides or carbon oxides under severe condition. From Table 4, it is clear that there are more indanone over Cat. No. 3 & 4 and more others over Cat. No. 2 in comparison with other catalysts. Those products are considered to be decomposed to carbon oxides under severe condition. On the other hand, Cat. No. 1 is so active that MA formed might be decomposed to carbon oxides.

## CONCLUSIONS

In tests of V-O, V-P-O, V-Mo-O, V-Mo-P-O and V-Ag-O for CPD to MA, V-Ag-O shows the highest selectivity. Redox mechanism could be employed to interpret the oxidation of CPD over above catalysts. The additives are thought to moderate the tendency of an oxide to donate

its oxygen.

## NOMENCLATURE

AV   :  average of vanadium valence in catalyst
C   :  conversion, moles of CPD reacted/moles of CPD in feed $\times$ 100(%)
$F_c$   :  fraction of CPD unconverted
k, k′   :  reaction rate constants
n   :  order of reaction
$P_c$   :  partial pressure of CPD
$r_c$   :  reaction rate of CPD
S   :  selectivity calculated on carbon atom basis (%)
$S_{MA}$   :  selectivity to MA, moles of MA produced/mole of CPD reacted $\times$ 4/5 $\times$ 100 (%)
T   :  time factor, weight of Cat./feeding rate (g. sec. mole$^{-1}$)
$[V^{5+}]$   :  concentration of $V^{5+}$ in catalyst (mmole/g)
$Y_{MA}$   :  yield of MA, weight of MA produced/weight of CPD in feed $\times$ 100 (%)

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