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THE EFFECT OF SILVER ADDITION ON CATALYTIC PROPERTIES OF VANADIA CATALYST FOR OXIDATION OF CYCLOPENTADIENE

Ki-Won Jun and Kyu-Wan Lee*

Catalysis Research Division, Korea Research Institute of Chemical Technology,
P. O. Box 9, Daedeog-Danji, Taejeon 305-606, Korea

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Abstract—The catalyst systems of silver-added vanadia for selective oxidation of cyclopentadiene were studied. As silver of the amount below Ag/V atomic ratio of 0.1 being added into vanadia, the catalytic selectivity for the formation of maleic anhydride was improved. This modifying effect was seemed to be related to the weakening of oxide property of vanadia with the formation of phase AgV_6O_{15} in vanadium pentoxide. However, the large-amount addition of silver caused the catalyst to lose oxide property, thereby, made the catalytic selectivity poor. Mars and van Krevelen model was applied for kinetics study. The results indicate that the reoxidation of catalyst was the rate determining step and that the addition of silver lowers the activation energy in cyclopentadiene oxidation.

INTRODUCTION

Partial-oxidation reactions catalyzed by transition-metal oxides are some of the most widely applied processes for converting hydrocarbons into valuable chemical intermediates. The catalytic oxidation of hydrocarbons such as n-butane, n-butene and benzene has been used commercially to produce maleic anhydride (MA).

Cyclopentadiene (CPD), which is one of the major components of C_5 fractions obtained from steam cracking of naphtha, also can be oxidized into MA with high selectivity [1-8].

Slavinskaya and coworkers [2, 3] found that silver-added vanadium pentoxide was an efficient catalyst for the CPD oxidation showing the highest selectivity at atomic ratio of $V : Ag = 1 : 0.003$. They attributed the modifying of catalytic behavior to the heterogeneity in oxygen bond energies due to formation of AgV_7O_{18} and AgV_6O_{15} phases.

To better understand the modification on silver addition, in this work, the system silver-added vanadia was characterized with x-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and scanning electron microscopy (SEM) and kinetics study for oxidation of cyclopentadiene was also done.

EXPERIMENTAL

1. Catalyst Preparation

The source material of active components, ammonium vanadate and silver nitrate, were dissolved in distilled water. For the dissolution of ammonium vanadate, exess oxalic acid was added as reducing agent. Support materials, α-alumina, was added to aqueous solution of active components and the mixture was concentrated to paste consistency with vigorous stirring. The amount of α-alumina was 5 wt/wt of active components. The paste was dried overnight and calcined in air at 500℃ for 3 hours. The catalysts were crushed and sieved.

The prepared catalysts and their surface areas of catalysts are listed in Table 1. The surface areas of catalysts were determined by the BET method.

2. Catalyst Characterization

X-ray diffraction measurements were performed on a Rigaku D/MAX III B diffractormeter with a Cu target.

Diffuse reflectance spectra of the catalysts were observed in 200-850 nm range by Shimadzu UV-240 Spectrophotometer.

Scanning electron microscopic studies were perform-

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*To whom all correspondences should be addressed.

Table 1. The prepared catalysts and their surface areas

Catal. no.	Active components (atomic ratio)		Surface area (m^2/g)
1	V		1.6
2	V-Ag	(1 : 0.0015)	1.3
3	V-Ag	(1 : 0.003)	1.0
4	V-Ag	(1 : 0.006)	1.4
5	V-Ag	(1 : 0.03)	1.4
6	V-Ag	(1 : 0.1)	1.3
7	V-Ag	(1 : 0.3)	1.8

ed on a JEOL JSM-840A scanning electron microscope.

3. Reaction Apparatus and Methods

CPD oxidation experiments were performed in a conventional flow reactor system under atmospheric pressure. Two types of reactor were used: Pyrex reactor (26 cm×1.4 cm I.D.) was used for the measurement of catalytic selectivity. Stainless steel reactor (30 cm×1.05 cm I.D.) was used for the measurement of kinetics. This reactor was divided into five individual heating zones, and each heating zone was controlled independently.

The catalysts were diluted with quartz particles and placed between zones of quartz particles. A reactant mixture was prepared by saturating air with CPD at constant temperature, and diluting it with dried air to give appropriate CPD concentration. The experimental conditions were: flow rate of gas=75-670 ml/min, catalyst amount=0-3g, CPD concentration=0.3-1.0 mole%, and reaction temperature=300-480℃.

Effluent gases from reactor was splitted into two streams. The major stream was sent into cold traps and the minor stream was made to pass via a heated line and gas sampling valve for the on-line analysis.

The analysis of the inlet and outlet gases of the reactor was carried out by two gas chromatographs. The organic reactant and products were analyzed by a Shimadzu GC-8APF gas chromatograph equipped with TENAX-GC column with flame ionization detection. After removing most of organic reactant and products in cold traps, the gaseous products CO and CO_2 were analyzed by a Shimadzu GC-8APT gas chromatograph equipped with Carbosieve-S and Porapak-Q columns with thermal conductivity detection.

RESULTS

1. Catalyst Characterization

Structural characterization of silver-promoted vanadia was conducted by X-ray diffraction. XRD patterns of catalysts of No. 4-7 were shown in Fig. 1. Silver addition less than Ag/V=0.006 did not change the patterns of Al_2O_3 and V_2O_5. As silver addition was increased, the structure of AgV_6O_{15} was observed, and then the catalyst of Ag/V=0.3 appeared to be composed of two phases of Al_2O_3 and AgV_6O_{15}.

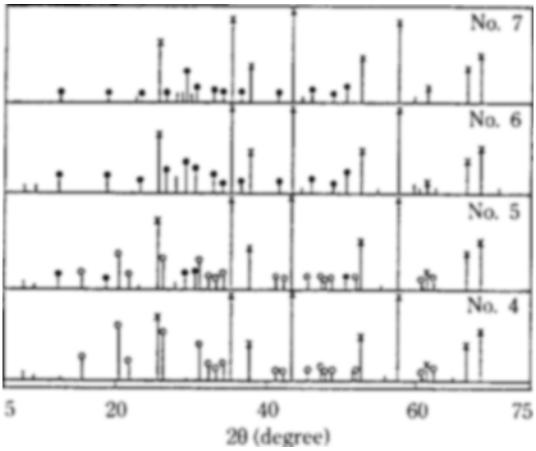


Fig. 1. X-ray diffraction patterns of catalysts. ×, α-Al_2O_3; ○, V_2O_5; ●, AgV_6O_{15}.

UV-visible diffuse reflectance spectra was obtained for silver-added vanadia and they are shown in Fig. 2. The vanadia catalysts exhibits absorption edge in the wavelength region of 500-600 nm. The absorption edge in the 500-600 nm region is assigned to a charge-transfer transition from O^{2-} to V^{5+} [9]. As the silver content increased, this absorption edge decreased. Thereafter, at high silver-content of Ag/V=0.3 the spectrum of catalyst shows little absorption edge. These results indicate that silver addition weakens the oxide character of vanadia.

The absence of absorption bands for one-electron d-d transitions in 600-800 nm region [9] indicates that the amount of V^{4+} ions is small for all catalysts shown.

The representative results of SEM analysis are shown in Fig. 3. Seeing Fig. 3 (a) (No. 1), round-shaped particles and acicular form of vanadia appears on larger particles of α-alumina. In Fig. 3(b) (No. 6), the round-shaped particles of active component on alumina are little different from that of sample No. 1. However, the catalyst of Ag/V=0.3 (No. 7) shows rod-like form that is different from normal vanadium pentoxide. This indicates that there is structural change of active component system in much silver-addition of Ag/V=0.3.

2. Testing Results of Catalytic Performance

Product distributions in the CPD oxidation were complex resulting in many kinds of products, including MA, phthalic anhydride, CO, CO_2, cyclopentenone, cyclopentenedione, pyrone, indanone and several uniden-

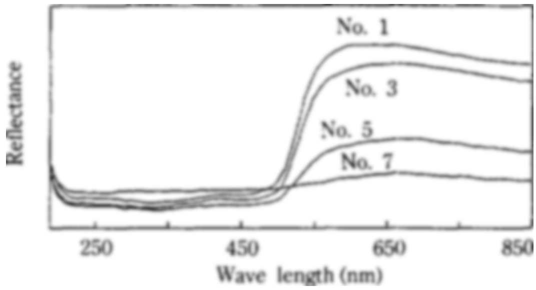
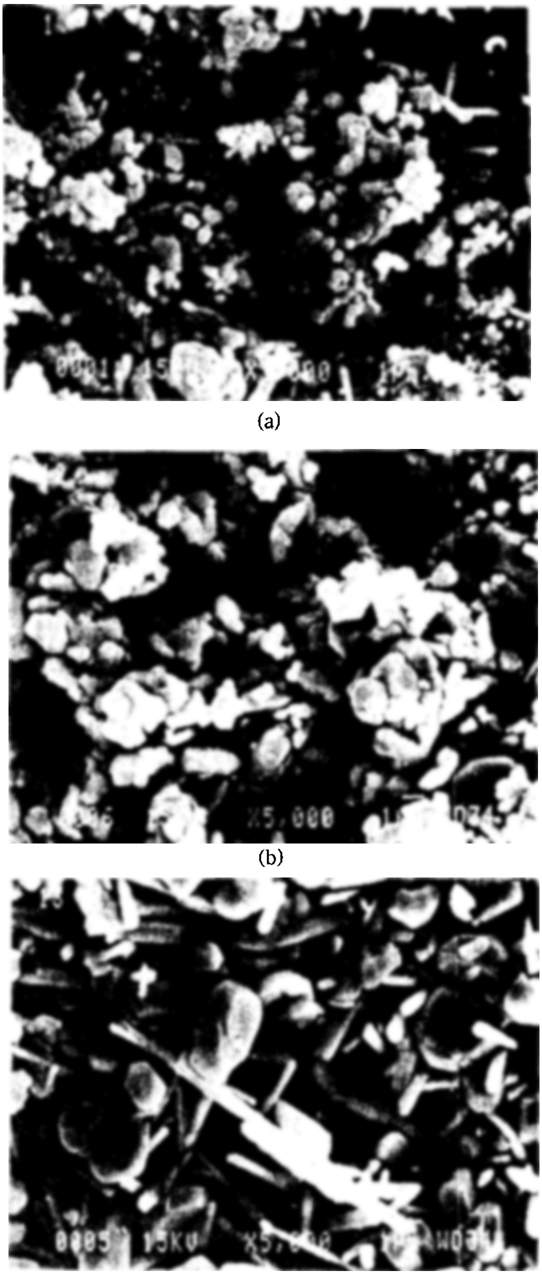


Fig. 2. Diffuse reflectance spectra of catalysts.


(a)

(b)

(c)

Fig. 3(a). Scanning electron micrograph of catalyst No. 1.
(b). Scanning electron micrograph of catalyst No. 6.
(c). Scanning electron micrograph of catalyst No. 7.

tified compounds. The maximum yield to MA was obtained at complete or almost complete conversion of CPD. At that time, PA was a major byproduct. A typical result is shown in Fig. 4.

The maximum selectivities over silver-promoted catalysts were listed in Table 2. As silver of small amount of Ag/V = 0.0015 being added into vanadia, the selectivity was a little increased. The catalyst vanadia-silver of Ag/V = 0.003 (No. 3) showed about 10% increase and the catalyst of Ag/V = 0.006 (No. 4) showed about 9% increase in the selectivity as compared with vanadia (No. 1). As seeing Table 2, at silver addition of the amount below Ag/V = 0.1, the catalytic selectivity for the formation of MA was improved. However, much silver addition of Ag/V = 0.3 lowered the selectivity to half degree.

3. Kinetic Results

In the case of butene to MA redox mechanism was occasionally applied to kinetic studies [10-12]. In this study this mechanism, so-called Mars and van Krevelen model, was employed to interpret the kinetics of CPD oxidation.

The rate expression according to this model is derived as follows:

(1) The step of oxidation of hydrocarbon with reduction of oxide in oxidized form:

$$r_1 = k_H P_H (1-\theta) \tag{1}$$

(2) The step of reoxidation of reduced oxide by oxygen:

$$r_2 = k_0 P_0^n \theta \tag{2}$$

Approximation of steady state gives

$$r = \frac{1}{(1/k_H P_H) + (\beta/k_0 P_0^n)} \tag{3}$$

For the hydrocabon oxidation reactions, their data were fitted by n = 1, therefore, the linearized form of Eq. (3) is

$$\frac{1}{r} = \frac{1}{k_H P_H} + \frac{1}{k_0' P_0} \tag{4}$$

In order for experimental data to agree with Eq. (4), a plot of 1/r vs. $1/P_H$ should gives a straight line

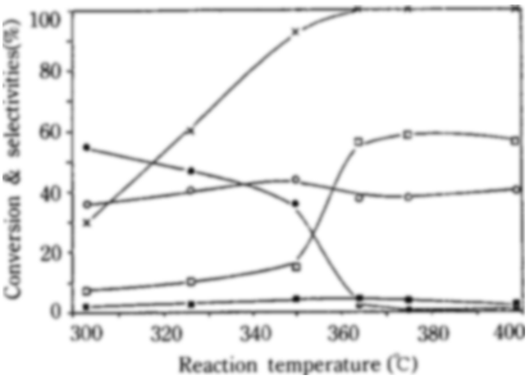


Fig. 4. Plots of conversion and selectivities vs. reaction temperature on No. 3 catalyst. ×, conversion; □, selectivity to maleic anhydride; ■, selectivity to phthalic anhydride; ○, selectivity to carbon oxides; ●, selectivity to others.

Table 2. The maximum selectivity over V_2O_5-Ag catalyst

Catal. no.	V : Ag (atomic ratio)	Temperature[a] (℃)	Select.[b] (mol%)
1	1 : 0	350	48.9
2	1 : 0.0015	376	50.6
3	1 : 0.003	375	58.4
4	1 : 0.006	350	57.2
5	1 : 0.03	350	52.0
6	1 : 0.1	361	50.8
7	1 : 0.3	376	25.1

[a] Other reaction conditions are: GHSV = 5000 hr^{-1}, CPD concentration = 0.6 mol%.

[b] Selectivity was defined as the percentage of produced MA per reacted CPD.

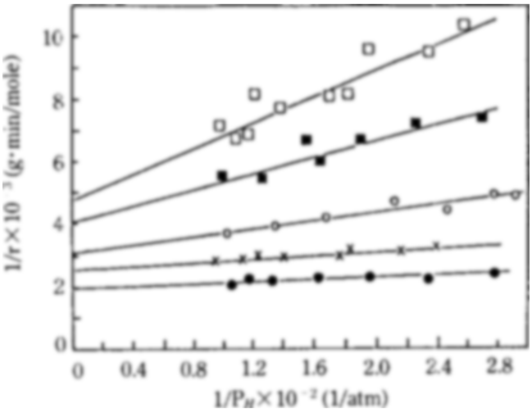


Fig. 5. Plots of 1/r vs. $1/P_H$ for V_2O_5 catalyst (No. 1). □, 330℃; ■, 340℃; ○, 350℃; ×, 360℃; ●, 370℃.

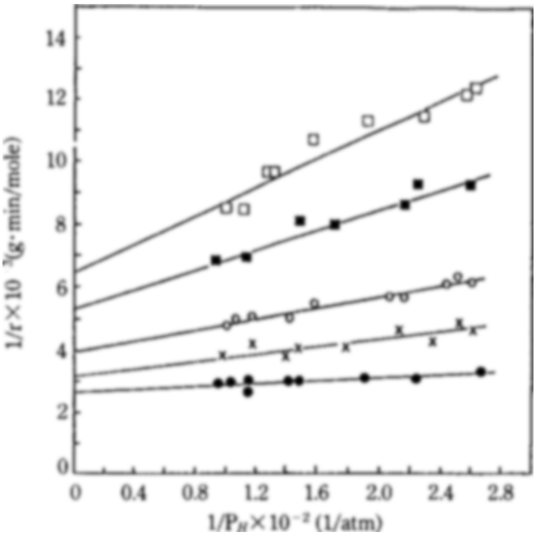


Fig. 6. Plots of 1/r vs. $1/P_H$ for V_2O_5-Ag catalyst (No. 3). □, 330℃; ■, 340℃; ○, 350℃; ×, 360℃; ●, 370℃.

Table 3. Estimated kinetic parameters

Catalyst No. 1 (V_2O_5)

T (℃)	$k_H\times10^2$	$k_0'\times10^3$	$k_HP_H\times10^4$	$k_0'P_0\times10^4$	θ
330	4.7	1.0	3.3	2.1	0.61
340	7.6	1.2	5.3	2.5	0.68
350	15.4	1.6	10.8	3.3	0.77
360	33.5	1.9	23.4	4.0	0.86
370	72.4	2.4	50.7	5.0	0.91

Catalyst No. 3 (V_2O_5-Ag)

T (℃)	$k_H\times10^2$	$k_0'\times10^3$	$k_HP_H\times10^4$	$k_0'P_0\times10^4$	θ
330	4.4	0.7	3.1	1.6	0.67
340	6.4	0.9	4.5	1.9	0.71
350	11.7	1.2	8.2	2.5	0.77
360	18.3	1.5	12.8	3.1	0.81
370	43.3	1.8	30.3	3.8	0.89

and the slope becomes $1/k_H$ and the intercept becomes $1/k_0'P_0$.

Since experimental error could not be ignored at low total conversion not exceeding 10%, semi-differential reaction at total conversion of 10-20% was performed for this kinetic study. The initial rate was obtained by iteration method using empirical model [13].

It is verified by plotting 1/r vs. $1/P_H$ that CPD oxidation follows redox mechanism (Figs. 5 and 6). From the results and Figs. 5 and 6, kinetic parameters have been estimated and are given in Table 3. The values of k_HP_H and $k_0'P_0$ in Table 3 indicate reduction rates and oxidation rates of catalyst, respectively. It is read-

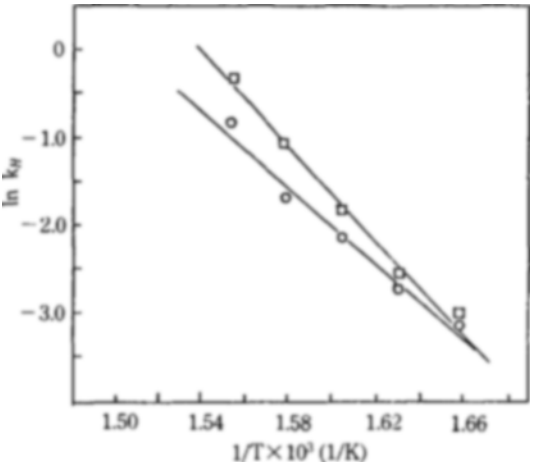


Fig. 7. Arrhenius plots for k_H. □, catalyst No. 1; ○, catalyst No. 3.

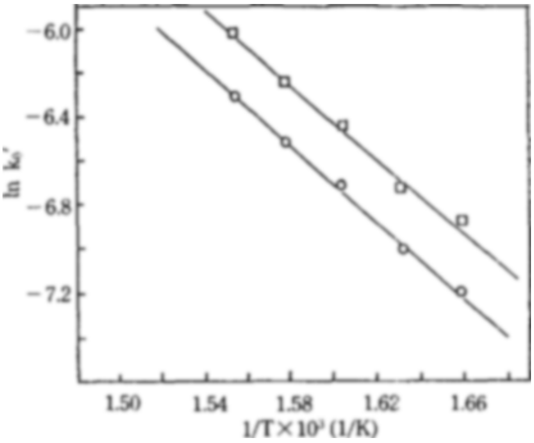


Fig. 8. Arrhenius plots for k_0'. □, catalyst No. 1; ○, catalyst No. 3.

ily seen that the reduction of catalyst is faster than the oxidation of catalyst in this reaction, therefore, the oxidation of catalyst is rate determining step. From Arrhenius plots of k_H and k_0' (Figs. 7 and 8), activation energies of reduction and oxidation of catalysts have been obtained as shown in Table 4.

DISCUSSION

It is difficult to understand the correct mechanism of promoting effect because small-amount addition of silver (V : Ag = 1 : 0.003) gives little information of instrumental analysis. However, it can be deduced from the characterization of higher silver-contents. It seems that the promoting effect is related with adding new phase into vanadium pentoxide as can be seen in the XRD results. It appears that formation of new phase causes the change of electronic property as can be seen in the DRS results. Since AgV_6O_{15} phase was found in this study, it is most likely that the formation of AgV_6O_{15} phase plays a role of improving the selectivity. As previously stated in the result of DRS, the formation of new phase would weaken of too strong oxide-property to do selective oxidation. The poor catalytic performance of sample No. 7 (Ag/V = 0.3) seems to be related with little absorption edge of DRS. The large-amount addition of silver may cause vanadia to lose oxide property, which is able to offer hydrocarbon lattice oxygen as selective oxidizer. That fact, the active component of catalyst No. 7 is quite different from vanadium oxide, is supported by the SEM results.

Table 4. Activation energies and preexponential factors

Step	E_a (Kcal/mole)	A (mole/g·atm·min)
Reduction of catalyst		
Catalyst No. 1	53.5	9.64×10^{17}
Catalyst No. 3	43.3	1.85×10^{14}
Oxidation of catalyst		
Catalyst No. 1	17.0	1.42×10^{4}
Catalyst No. 3	17.5	1.59×10^{4}

From this kinetic results, it was concluded that the oxidation of catalyst is rate determining step. This result is similar to the case of benzene oxidation that was reported by Tufan and Akgerman [14]. As seeing Fig. 7, there appears a little deficiency of linearity. This may be caused by different reduction degrees of vanadia surfaces which are dependent on reaction temperature.

As comparing kinetic results over catalysts No. 1 and No. 3, it is apparent that the addition of silver decreases the activation energy for the reduction step of catalyst. The reduction of catalyst corresponds to the oxidation of hydrocarbon. This fact suggests that addition of silver lowers the energy of transition state in CPD oxidation, for that reason the more mild oxidation would occur over silver-added catalyst.

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NOMENCLATURE

k_H : reaction rate constant for oxidation of hydrocarbon

k_0 : reaction rate constant for reoxidation of oxide
k_0' : k_0/β
n : order of reaction
P_H : partial pressure of hydrocarbon
P_{H0} : initial P_H
P_O : partial pressure of oxygen
r : reaction rate
r_1 : reaction rate for oxidation of hydrocarbon
r_2 : reaction rate for reoxidation of oxide
T : reaction temperature [℃]
β : moles O_2 consumed per mole of hydrocarbon reacted
θ : fraction of active sites in reduced state

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