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Liquid Phase Diacetoxylation of 1,3-Butadiene with Pd–Te–C Catalyst

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The catalytic properties of Pd–Te bimetallic system supported on charcoal (Pd–Te–C) for liquid-phase diacetoxylation of butadiene was studied in comparison with other heterogeneous (Pd–C, Pd–As–C, Pd–Bi–C, Pd–Sb–C, Pd–Se–C, Pd–Te–Al_2O_3, or Pd–Te–SiO_2) or homogeneous [$Pd(OAc)_2$–$Cu(OAc)_2$–KOAc or $PdCl_2$–$CuCl_2$–KOAc] palladium-based catalysts. The highest activity for 1,4-diacetoxylation was obtained with the Pd–Te–C catalyst prepared from $Pd(NO_3)_3$ and TeO_2 dissolved in aqueous nitric acid solution, for all the catalysts studied. The reaction seems to proceed catalytically on the surface of this supported bimetallic system, and its active species is suggested to be some palladium tellurides, in which Pd serves by a redox mechanism, being coupled with Te. The Pd–Te–C system catalyzed the direct diacetoxylation of butadiene, which is considered to proceed via π-allyl-type intermediate. The use of the ratio of Pd:Te $\simeq$ 10:1 on charcoal is the most effective; a higher content in Te results in a lowering of the activity, possibly brought on by the unfavorable deposition of tellurium oxides on the catalyst surface. With the Pd–Te–C system, the following values of selectivities of diacetoxybutenes were obtained: *trans*-1,4-diacetoxy-2-butene, 75%; *cis*-1,4-diacetoxy-2-butene, 14%; and 3,4-diacetoxy-1-butene, 10%.

I. INTRODUCTION

1,4-Butanediol is a useful industrial product as a comonomer for producing butanediol polyterephthalate or as a raw material for making tetrahydrofuran, pyrollidone, etc. For its industrial production from butadiene, several processes have been proposed: hydrogenation of the polyperoxide formed by the autoxidation of butadiene (*1*) and hydrogenation followed by the hydrolysis of 1,4-diacetoxy-2-butene (1,4-DAB) prepared by the diacetoxylation of butadiene. 1,4-DAB can be obtained stoichiometrically by the reaction of butadiene with cupric chloride (*2*) or thallium (III) acetate (*3*) in the presence of sodium acetate, or by the oxidation of butadiene with SeO_2 in acetic acid (*4*), or catalytically in the presence of Wacker-type systems based on palladium. Recently, several patents have claimed the use of homogeneous metal salts systems containing Pd, Cu, and alkali metal (*5*) or heterogeneous catalysts where palladium associated with antimony, bismuth, selenium, or tellurium are deposited on charcoal (*6–8*). From the patent literature, it appears that palladium coupled with tellurium and supported on charcoal (Pd–Te–C) is the most effective catalyst for the liquid-phase 1,4-diacetoxylation of butadiene (*7, 8*). However, no details of this catalyst system have been published except for the patent literature above. Here, we study the catalytic

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TABLE 1

Concentration of Pd and Te in Pd–Te–C Catalyst

Catalyst No.	Calculated value (g-atom/g-cat × 10^{-4})		Experimental value (g-atom/g-cat × 10^{-4})	
	Pd	Te	Pd	Te
1	3.0	0.75	3.3	0.78
2	6.0	1.5	5.8	1.1

properties of Pd–Te–C systems in comparison with other heterogeneous or homogeneous palladium-based catalysts.

II. EXPERIMENTAL METHODS

1. Catalysts. The catalysts were prepared according to the patent literature (*7, 8*), i.e., the palladium salt was dissolved together with the cocatalyst (salt or oxide of Te, Se, As, Sb, or Bi) in water in the presence of a strong acid (HCl or HNO_3). The obtained solution was poured on the dried granular support and boiled at about 100°C for 6 hr. After evaporation of water *in vacuo*, the supported catalyst was dried for 2 hr at 150°C under N_2 stream and then reduced at 200°C for 2 hr and at 400°C for 4 hr under N_2 stream saturated with methanol.

As a support, we used either charcoal (Prolabo, surface area 1140 m^2/g) pretreated with 30% aqueous HNO_3 solution at 100°C for 6 hr, on γ-alumina (Procatalyse, surface area 194 m^2/g) or silica gel (Procatalyse, surface area 203 m^2/g). These supports were pulverized and used as 0.2- to 0.4-mm particle size powders.

The concentration of supported metals in the two typical Pd–Te–C catalysts prepared from $Pd(NO_3)_3$, TeO_2, and charcoal by the above-mentioned method was determined by X-ray spectroscopy, and the results are shown in Table 1.

2. Apparatus and procedure. The oxidations were carried out by two different procedures, using either a gas-sealed system or a gas-flowed system. In the former case, we used the apparatus shown in Fig. 1. Oxygen and butadiene were stored in two different gas burettes. In a typical procedure, acetic acid and the catalyst were put into a glass reactor and frozen at −78°C. After vacuuming the reactor with a rotary pump, a determined quantity of oxygen was introduced and then the reaction mixture was heated at the requested temperature. Butadiene was then added. After the equilibrium of solubilization of butadiene in acetic acid was reached, the reaction was started and oxygen and butadiene uptakes were measured simultaneously. At the beginning of the reaction, the total pressure in the reactor was fixed at 960 mm Hg, and the ratio of the butadiene and oxygen partial pressures was maintained constant during the reaction by glc control of the gas-phase composition and adjustment of the respective levels in the gas burettes.

In the gas-flowed system, oxygen and butadiene at constant flow rates were bubbled into the reaction mixture containing the catalyst and acetic acid.

The reaction mixture was then analyzed after cooling and elimination of the catalyst by filtration.

3. Analysis. The oxidized products were isolated from the reaction mixture using

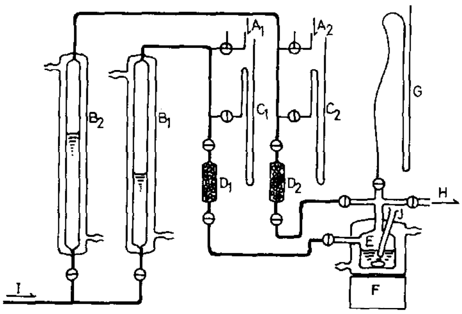


FIG. 1. Reaction apparatus. A_1, A_2, feed of gases (1:oxygen, 2:butadiene); B_1, B_2, gas burettes; C_1, C_2, manometers for control; D_1, D_2, columns of SiO_2; E, reactor; F, magnetic stirrer; G, manometer; H, rotary pump; I, water; J, thermometer.

gas–liquid chromatography on a preparative scale (Thomson THN 101, column: Carbowax 20M) and identification of products was done by comparison of ^{13}C NMR spectra (Varian CFT 20) and mass spectra (AEI MS 12) with authentical samples. 3,4-Diacetoxy-1-butene (3,4-DAB), *cis*-1,4-diacetoxy-2-butene (*cis*-1,4-DAB), and *trans*-1,4-diacetoxy-2-butene (*trans*-1,4-DAB) were detected as the main products of the reaction. A quantitative analysis was performed by an Intersmat IGC 12 M gas chromatograph fitted with a 2-m-long column FFAP 15% on chromosorb NHDMS 80/100.

The concentrations of supported Pd and Te were determined using the X-ray spectrometer Phillips PW 1410. The surface areas of the catalysts were measured by BET method using nitrogen. X-Ray diffraction diagrams of the catalysts were recorded on a conventional Phillips unit. X-Ray photoelectron spectra were measured by a du Pont ESCA 650 B using monochromatic Al*Kα* radiation. All binding energy values were referenced to C 1s (285.0 eV). In this calibration method, there is the fear of undesirable broadening or chemical shifts of the C 1s line arising from the coexistence of contaminant hydrocarbon and the charcoal. However, such a phenomenon did not occur to the point of causing a disturbance in the calibration. The distributions of Pd and Te in the catalyst particles were recorded on a Shimazu electron probe X-ray microanalyzer, using Pd*Lα* and Te*Lα* lines. The samples were fixed on a sample holder with epoxy resin, then polished, and a thin carbon film was plated on its surface by vacuum evaporation. The amount of dissolved Pd in the reaction solution was determined using the Perkin Elmer 400 atomic absorption spectrophotometer.

III. RESULTS

Figure 2 shows typical plots of oxygen and butadiene uptakes versus time during a representative liquid-phase oxidation using a Pd–Te–C catalyst. The partial pressure ratio of butadiene and oxygen was maintained at about 3:2. No induction period was observed. Since dissolution of the catalyst does not occur in the liquid phase (*vide infra*), most of the reaction seems to proceed on the catalyst surface rather than in solution. As the catalytic activity decayed gradually, only the initial rates were determined from the maximum slopes of gas uptakes.

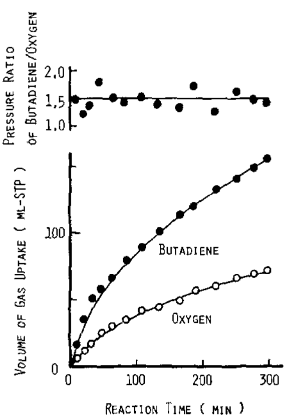


FIG. 2. Uptake of gases in oxidation with Pd–Te–C catalyst. Reaction temperature, 90°C; catalyst Pd–Te–C (Pd, 0.3×10^{-3} g-atom/g-cat; atomic ratio of Te/Pd, $\frac{1}{8}$), 1.00 g; acetic acid, 30 ml; partial pressure ratio of butadiene/oxygen, 60/40.

1. *Influence of the Nature of the Catalyst*

Table 2 lists some representative results obtained with several heterogeneous bimetallic systems (Expts 3 to 12) in comparison with homogeneous Pd–Cu couples (Expts 1 and 2) under the same conditions.

For homogeneous catalysts (Expts 1 and 2), higher rates and selectivity in 1,4-diacetoxylation were observed using metal acetates, in comparison with metal chlorides. In the latter case, most of the metal chlorides remained insoluble during the reaction, whereas metal acetates dissolved completely in acetic acid. The activities of several heterogeneous catalysts prepared from $PdCl_2$ were compared.

TABLE 2

Acetoxylation of Butadiene with Various Binary Metal Catalysts[a]

Catalyst	Reaction rate (10^{-5} mol/liter·sec·g-cat)		DAB						Reaction time (min)	Expt No.
			Yield (10^{-3} mol)			Selectivity (%)				
	Butadiene	Oxygen	*trans*-1,4	*cis*-1,4	3,4	*trans*-1,4	*cis*-1,4	3,4		
$Pd(OAc)_2 \cdot Cu(OAc)_2 \cdot KOAc$[b]	1.07	0.30	3.23	0.36	1.25	43.5	4.9	16.9	380	1
$PdCl_2 \cdot CuCl_2 \cdot KOAc$[b]	0.42	0.15	Trace	Trace	0.16	—	—	15.1	360	2
Pd-C[c]	0.23	0.10	0.02	Trace	0.16	10.5	—	69.5	360	3
Pd-As-C[c]	0.22	0.10	0.20	Trace	0.35	27.3	—	47.7	360	4
Pd-Sb-C[c]	0.40	0.17	0.60	0.13	0.35	44.3	9.6	26.0	360	5
Pd-Bi-C[c]	0.40	0.15	0.57	Trace	0.64	37.4	—	42.0	360	6
Pd-Se-C[c]	0.95	0.45	1.36	0.26	0.66	47.8	9.1	23.2	360	7
Pd-Te-C[c]	2.60	0.97	2.27	1.63	0.60	42.9	30.8	11.3	300	8
Pd-Te-Al_2O_3[c]	0.70	0.29	0.54	0.01	0.35	47.8	0.9	31.0	360	9
Pd-Te-SiO_2[c]	0.19	0.06	Trace	Trace	Trace	—	—	—	360	10
Pd-Se-C[d]	1.80	0.79	3.01	0.55	0.67	62.4	11.4	13.9	300	11
Pd-Te-C[d]	3.42	1.30	3.60	1.45	0.67	62.9	25.3	11.7	300	12

[a] Reaction temperature, 90°C; total pressure, 960 mm Hg; butadiene/oxygen = $\frac{3}{2}$; AcOH, 30 ml; catalyst, 1 g.

[b] Amount of metals used: Pd, 0.3×10^{-3} g-atom; Cu, 6.0×10^{-3} g-atom; K, 15×10^{-3} g-atom.

[c] Prepared from $PdCl_2$ and oxide of second component dissolved in HCl aq. soln., Concentration of metals: Pd, 0.3×10^{-3} g-atom/g-cat; second component; 0.075×10^{-3} g-atom/g-cat.

[d] Prepared from $Pd(NO_3)_2$ and oxide of second component dissolved in HNO_3 aq. soln. Concentration of metals is same as in footnote *c*.

Palladium alone supported on charcoal showed a very low activity, together with a very low selectivity in 1,4-DAB (Expt 3). However, the oxidation rates and the selectivity in 1,4-DAB were improved by the addition of a second component, i.e., As, Sb, Bi, Se, or Te (Expts 4 to 8). The best results were obtained by using the Pd-Te association (Expt 8). The two isomers of 1,4-DAB, i.e., *cis* and *trans*, were obtained, and a greater amount of the *cis*-form was observed with the Pd-Te-C catalyst in contrast to the other systems. Experiments 8 to 10 show that charcoal is the best support for the Pd-Te couple. The use of γ-alumina or silica gel results in a markedly inferior activity. When the latter two supports were used, a certain amount of Pd was detected in the liquid phase after the reaction, i.e., ca. 0.18 $\times 10^{-3}$ g-atom/liter for the Pd-Te-Al_2O_3 catalyst (Expt 9) and ca. 0.22 $\times 10^{-3}$ g-atom/liter for the Pd-Te-SiO_2 catalyst (Expt 10) in comparison with a small value ($<0.004 \times 10^{-3}$ g·atom/liter) for the Pd-Te-C catalyst (Expt 8). Furthermore, by comparing the activities of Pd-Te-C catalyst with the homogeneous $Pd(OAc)_2$-$Cu(OAc)_2$-KOAc system at the same concentration of Pd, it appears that the heterogeneous catalyst is much more active and selective in 1,4-DAB formation than the homogeneous catalyst.

Experiments 11 and 12 show that the use of $Pd(NO_3)_3$ instead of $PdCl_2$ and nitric acid instead of hydrochloric acid as the solvent for the preparation of Pd-Te-C and Pd-Se-C catalysts results in higher activity for the 1,4-diacetoxylation of butadiene. Thus, it appears that the presence of chlorine ions is not useful for enhancing the activity of these catalysts. In the case of Pd-Se-C or Pd-Bi-C catalysts, there is the fear that an unfavorable deposit of metallic selenium or bismuth is brought on by the agglomeration of each atom during its preparation, since the melting point of Se or Bi is 220 or 271°C, respectively. Moreover, As_2O_3 is known to sublimate easily and therefore the Pd-As-C catalyst may contain less As than expected.

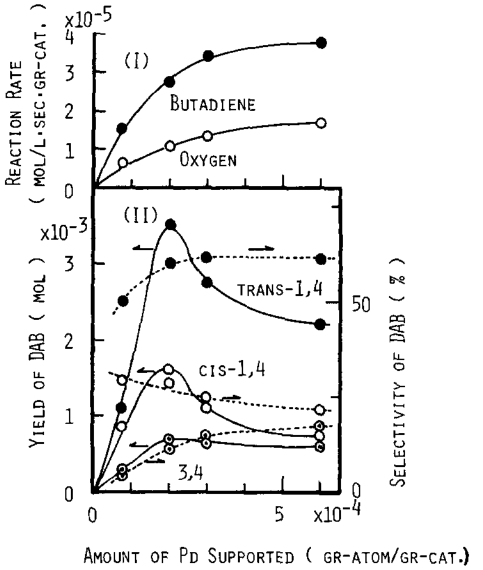


Fig. 3. Effect of metal concentrations on catalyst. Reaction temperature, 90°C; catalyst: Pd-Te-C (atomic ratio of Te/Pd, ¼), 1.00 g; acetic acid, 30 ml; partial pressure ratio of butadiene/oxygen, 60/40; reaction time, 300 min.

Hereafter, the study was followed using the most active catalyst, i.e., Pd-Te-C catalyst prepared from $Pd(NO_3)_3$ and TeO_2 dissolved in aqueous nitric acid.

2. *Behaviors of the Pd-Te-C Catalysts*

Figure 3 shows the dependence of the activity on the concentrations of metals supported. The oxidation rates increase by increasing the amount of palladium and tellurium supported on charcoal at a ratio Pd:Te = 4:1 until a concentration of about 3×10^{-4} g·atom Pd/g-cat is reached (I). However, the yields of diacetates, after 5 hr of reaction, reach maximum values at a concentration of about 2×10^{-4} g·atom Pd/g-cat and then decrease somewhat by further addition of metals (II). This inconsistency shows a greater disactivation of the catalyst containing more metal during the reaction.

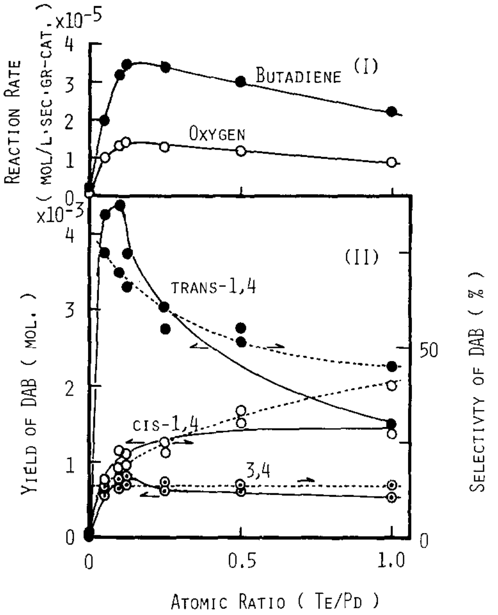


FIG. 4. Effect of addition of tellurium. Reaction temperature, 90°C; catalyst: Pd–Te–C (Pd, 0.3 × 10^{-3} g-atom/g-cat), 1.00 g; acetic acid, 30 ml; partial pressure ratio of butadiene/oxygen, 60/40; reaction time, 300 min.

The selectivity in *trans*-1,4-DAB and 3,4-DAB increases at the expense of *cis*-1,4-DAB when a greater amount of metal is supported on charcoal.

Figure 4 shows the influence of the Te:Pd ratio on the activity of the catalyst. When no tellurium is added, a very low activity is observed. However, the addition of a small amount of Te to the Pd–C catalyst results in a dramatic increase in activity. Though some inconsistency brought on by the disactivation of the catalyst is observed between the initial activity (I) and the yields of DABs (II), the activity reached a maximum at a ratio Pd:Te = 10:1 ~ 5:1. Especially, the highest yield of 1,4-DAB was obtained with the catalyst containing Pd:Te ≃ 10:1. This result seems at variance with the patent data where the active species was claimed as a definite compound of formula Pd_4Te (*8*). Increasing the Te:Pd ratio results in an interesting variation in the products distribution, i.e., a decrease in the formation of *trans*-1,4-DAB was observed together with an increase of *cis*-1,4-DAB. Here, thermal or catalytic isomerization between *cis*- and *trans*-1,4-DABs during the reaction may be considered. However, this possibility was defined by the following two experimental results: each of *cis*- and *trans*-1,4-DABs was treated with Pd–Te–C catalyst (Pd:Te = 4:1) in acetic acid at 90°C for 5 hr, with no isomerization. Thus, the presence of a greater amount of Te causes a lowering of the activity, together with a favoring of the formation of *cis*-1,4-DAB. A catalyst Te–C (Te: 3 × 10^{-4} g-atom/g-cat), prepared from TeO_2 dissolved in aqueous nitric acid, showed no activity.

In order to clarify the enhanced activity of the Pd–Te association, we tried to find the existence of definite compounds using X-ray diffraction of the catalyst. However, no diffraction line of palladium tellurides (Pd_4Te, Pd_3Te, Pd_2Te, PdTe, etc.) (*9*), metallic palladium, or tellurium, except some broad lines of fine graphite crystals, was found for most of the catalysts studied.

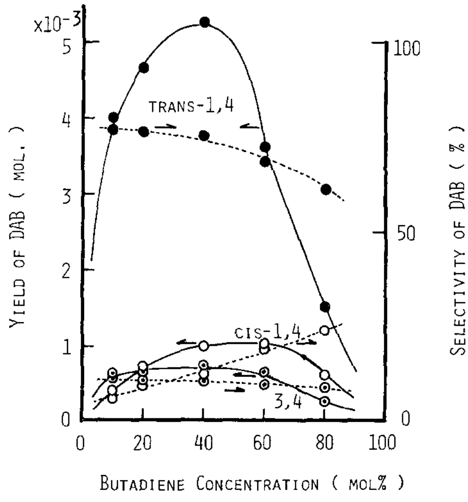


FIG. 5. Effect of composition in gas-phase. Reaction temperature, 90°C; catalyst: Pd–Te–C (Pd, 0.3 × 10^{-3} g-atom/g-cat; atomic ratio of Te/Pd, $\frac{1}{8}$), 1.00 g; acetic acid, 30 ml; reaction time, 100 min.

3. Influences of the Reaction Condition

The effects of partial pressure were studied by changing the gas phase composition. The products distribution are shown in Fig. 5. There was no oxidation observed without oxygen, and the reaction order with respect to oxygen calculated from the initial rate was about 1.0. The use of a higher concentration of butadiene resulted in a decrease in the *trans*-1,4- and 3,4-DABs or, contrarily, in an increase in the *cis*-1,4-DAB in its selectivity. Figure 6 shows the influences of the reaction temperature. A higher selectivity of *trans*-1,4-DAB together with a lower one of *cis*-1,4-DAB was obtained by increasing the temperature; however the selectivity of 3,4-DAB was approximately constant. An apparent activation energy obtained from the initial rate is about 6.4 kcal/mol. The results obtained by changing the amount of the catalyst are shown in Fig. 7. The reaction order with respect to the catalyst was about 0.8.

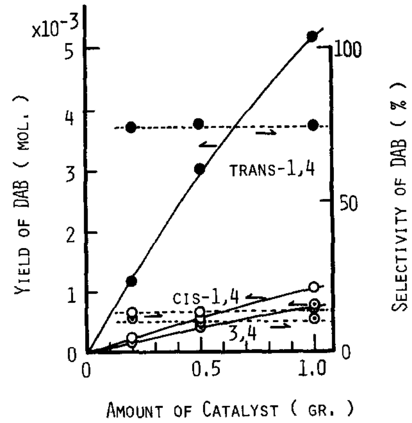


FIG. 7. Effect of catalyst concentration. Reaction temperature, 90°C; catalyst, Pd–Te–C (Pd, 0.3 × 10^{-3} g-atom/g-cat; atomic ratio of Te/Pd, $\frac{1}{8}$); partial pressure ratio of butadiene/oxygen, 40/60; reaction time, 100 min.

4. Reaction Results with the Gas-Flowed System

Figures 8 and 9 show the formations of DABs during the reaction for 40 hr with the gas-flowed system reactor, using respec-

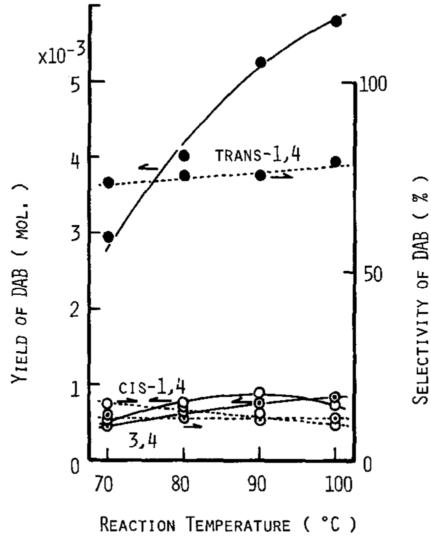


FIG. 6. Effect of reaction temperature. Catalyst: Pd–Te–C (Pd, 0.3 × 10^{-3} g-atom/g-cat; atomic ratio of Te/Pd, $\frac{1}{8}$), 1.00 g; acetic acid, 30 ml; partial pressure ratio of butadiene/oxygen, 40/60; reaction time, 100 min.

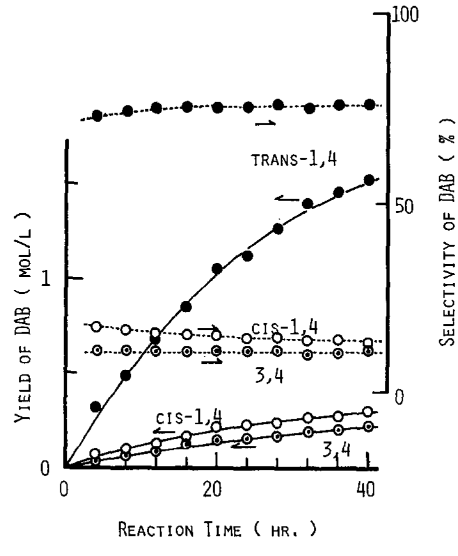


FIG. 8. Diacetoxylation with Pd–Te–C catalyst. Reaction temperature, 90°C; catalyst: Pd–Te–C (Pd, 0.3 × 10^{-3} g-atom/g-cat; atomic ratio of Te/Pd, $\frac{1}{8}$), 3.33 g; acetic acid, 100 ml; flow rate: butadiene, 50 ml/min; oxygen, 60 ml/min.

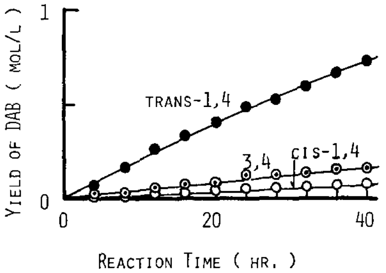


FIG. 9. Diacetoxylation with $Pd(OAc)_2 \cdot Cu(OAc)_2 \cdot KOAc$ catalyst. Reaction temperature, 90°C; catalyst: $Pd(OAc)_2$, 1×10^{-3} mol; $Cu(OAc)_2$, 20×10^{-3} mol; KOAc, 50×10^{-3} mol; acetic acid, 100 ml; flow rate: butadiene, 50 ml/min; oxygen, 60 ml/min.

tively Pd–Te–C catalyst and $Pd(OAc)_2$–$Cu(OAc)_2$–KOAc catalyst (for comparison) in the same amount of palladium. The use of Pd–Te–C resulted in the formation of almost only three DABs, but the metal acetates catalyst gave considerable amounts of some unidentified products together with the DABs as the main products. The distribution of three DABs, after a reaction time of 40 hr with the latter catalyst, was as follows: *trans*-1,4-DAB, 75%; 3,4-DAB, 18%; and *cis*-1,4-DAB, 7%. Evidently, Pd–Te–C catalyst shows a higher activity for 1,4-diacetoxylation than does the system of metal acetates. The activity of the Pd–Te–C catalyst dropped gradually during the reaction time, along with a small increase in *trans*-1,4-DAB and an oppositely small decrease in *cis*-1,4-DAB. The homogeneous catalyst of the metal acetates showed nearly a steady activity during the reaction. The initial rate of the formation of DABs was 8.1 mol/hr·g-atom Pd with the Pd–Te–C catalyst and 2.7 mol/hr·g-atom Pd with the metal acetates catalyst. After a reaction of 40 hr, the total yield of DABs was 205 or 97 mol/g-atom Pd with Pd–Te–C or $Pd(OAc)_2$–$Cu(OAc)_2$–KOAc, respectively.

III. DISCUSSION

From the results of Expts 3 to 8 (Table 2), the following order is obtained for the activity of the bimetallic catalyst prepared from $PdCl_2$:Pd–Te–C $\gg$ Pd–Se–C $>$ Pd–Sb–C $\geq$ Pd–Bi–C $>$ Pd–As–C. The order of the oxidation potential of each second component in aqueous solution is as follows: Se (Se–Se^{4+}, -0.740 V) $<$ Te (Te–Te^{4+}, -0.529 V) $<$ Bi (Bi–Bi^{3+}, -0.32 V) $<$ As (As–As^{3+}, -0.248 V) $<$ Sb (Sb–Sb^{3+}, -0.212 V) (*10*). Here, as mentioned already, the Pd–Se–C, Pd–Bi–C, or Pd–As–C catalysts may undergo unfavorable effects of melting or sublimation of the second component during preparation. Considering these disadvantages, the order of the catalytic activity may well coincide with the order of the oxidation potentials. It is suggested that the oxidation proceeds by a mechanism of Pd redox coupled with second component as reoxidizing agent, especially on Pd–Te–C or Pd–Se–C catalyst, as already accepted in Wacker-system catalyst of Pd–Cu couple. However, a positive charge on Pd in the oxidized state does not seem as large as observed with the Pd–Cu couple (i.e., Pd^{2+}), as is mentioned later.

The surface properties of the most active system, i.e., the Pd–Te–C catalysts prepared from $Pd(NO_3)_3$ and TeO_2 dissolved in aqueous nitric acid solution, was studied by X-ray photoelectron spectroscopy (XPS). The results are shown in Fig. 10. Pd on the Pd–C catalyst prepared from $Pd(NO_3)_3$ was mainly in the Pd(0) state (Pd $3d_{\frac{5}{2}}$, 335.8 eV) (*11*) and no PdO species (Pd $3d_{\frac{5}{2}}$, 337.0 eV) could be detected clearly. However, Pd was oxidized to several states by the addition of Te, and the higher ratio of Te:Pd resulted in the higher oxidation states of Pd. As for the energy level of Te $3d_{\frac{5}{2}}$, the following results were obtained. The main part of Te in the Te–C catalyst (containing no Pd) seems to be in Te(VI) state of TeO_3 (Te $3d_{\frac{5}{2}}$, 576.8 eV) (*12*), which is probably formed by dehydration of orthotelluric acid [$Te(OH)_6$] and reasonably remains on the catalyst because the trioxide is hardly

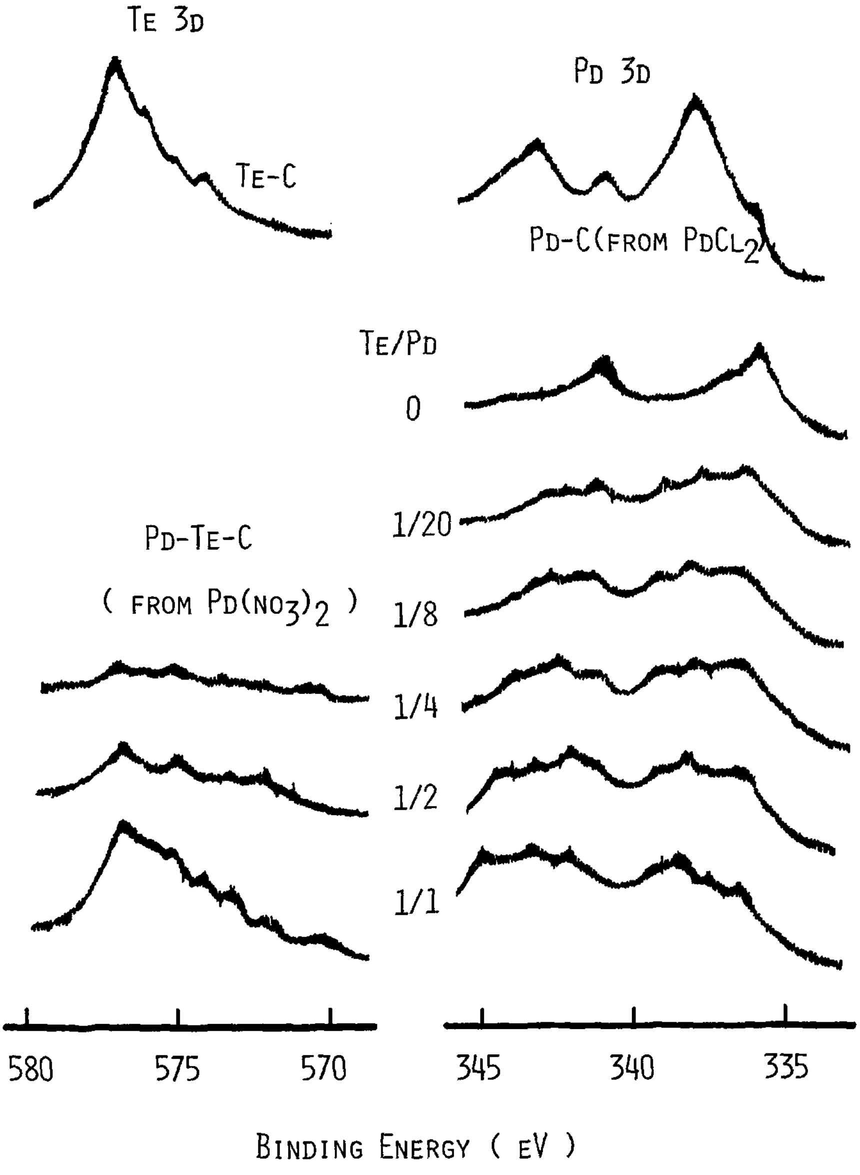


FIG. 10. Photoelectron spectra of Pd 3d and Te 3d on catalyst surface.

reduced even with hydrogen at high temperature (*13*). The orthotelluric acid may be formed when TeO_2 was treated with nitric acid during the impregnation. Other unidentified oxidation states of Te were also observed in this system. TeO_3 was also observed in the Pd–Te–C systems, especially in the system of higher Te content. The binary systems, however, also showed some reduced states of Te, which are of Te(0) (Te $3d_{\frac{5}{2}}$, 572.9 eV) (*12*) and of negative charges, though not clearly. The oxidized Pd and the reduced Te observed simultaneously in the Pd–Te–C systems may be attributed to the formations of intermetallic compounds, i.e., palladium tellurides Pd_nTe ($n = 1, 2, 3, 4,$ etc.) (*9*) on the catalysts. That is, in the

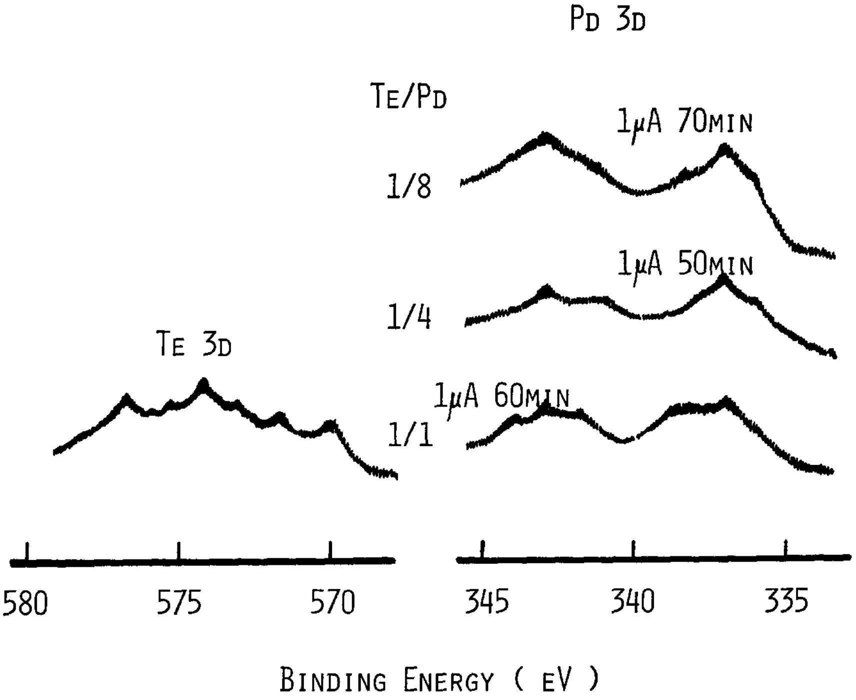


FIG. 11. Photoelectron spectra of Pd 3d and Te 3d on Ar^+ etched catalyst.

palladium tellurides, electronegative Te may deplete somewhat the electron density around Pd, withdrawing electrons from Pd. The depletion of electron density may become higher when n is smaller, and the several kinds of chemical shifts for Pd can be observed according to the values of n. Thus, it may be concluded that the increase in the ratio of Te:Pd gave rise to the higher oxidized state of Pd.

Spectra were measured for the samples from which layers of surface atoms had been removed by bombardment with Ar^+ ions (Fig. 11). With regard to the Pd 3d level, one level, i.e., signals at 336.9 eV ($3d_{\frac{5}{2}}$) and 432.8 eV ($3d_{\frac{3}{2}}$), among the several levels could be observed more readily by Ar^+ etching. This fact suggests that a certain palladium telluride exists more abundantly in the inner layers of the catalyst particle, as opposed to the several kinds of species being on its surface. At the surface of Pd–Te–C (Te:Pd = 1:1), a large amount of TeO_3 was observed as shown in Fig. 10. The signal of TeO_3 was remarkably weakened by the Ar^+ bombardment, and, accordingly, the TeO_3 may also be present on the surface.

The measurement results of the catalyst particles by electron probe X-ray microanalysis (EMX) are shown in Fig. 12. In most of the particles used, Pd and Te were detected even in the cores, to say nothing of the surface layers, though their X-ray intensities decreased somewhat on going toward the interior of the particles. The two metals were observed to distribute at an approximately constant ratio of Te:Pd from the surface to the inner layer in the catalysts of lower Te content. However, on increasing the Te content, more Te could be observed on the surface layers of the particle and also on its inner cavities, as shown in Te:Pd = 1:1.

Now, it may be concluded that several types of Pd_nTe exist on the Pd–Te–C catalysts together with some tellurium oxides, among which is TeO_3 localized on the surface skin of the catalyst of a higher Te content. No observation of any X-ray diffraction line indicates that the compounds are either very finely dispersed or amorphous. The active species of the Pd–Te–C catalysts is considered to be the palladium tellurides which serve as the coupled redox system of Pd–Te already mentioned. The Te–C system, on which TeO_3 was strongly detected, showed no activity. The surface area of the Pd–Te–C catalyst varied considerably when the supported amount of the metals (Fig. 13) or the atomic ratio of Te:Pd (Fig. 14) was changed. The value decreased proportionately to the supported amount. It is noteworthy that two types of dependence of the surface area to the Te:Pd ratio were observed, i.e., the values were nearly constant up to a ratio of about 1:8, but further addition of Te caused a decrease in the surface area proportional to the Te:Pd ratio. With the catalyst of Te:Pd > 1:8, a linearity was also observed between the lowering of the initial activity and the Te:Pd ratio [Fig. 4 (I)]. Therefore, the effective surface (probably including pores) might be reduced mainly by the deposition of TeO_3 when an excess amount of Te was added, resulting in a decrease in catalytic activity.

It was reported that, in the presence of oxygen and acetic acid, supported Pd is oxidized to $Pd(OAc)_2$ which may be the active species in the gas-phase acetoxylation of ethylene (*14*). However, the rate of the

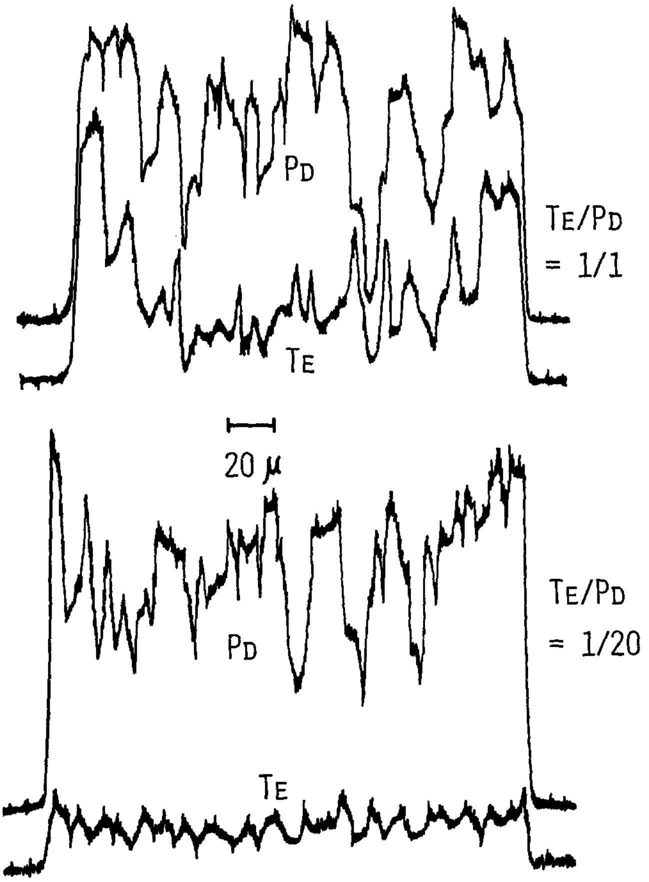


Fig. 12. EMX of catalyst particle.

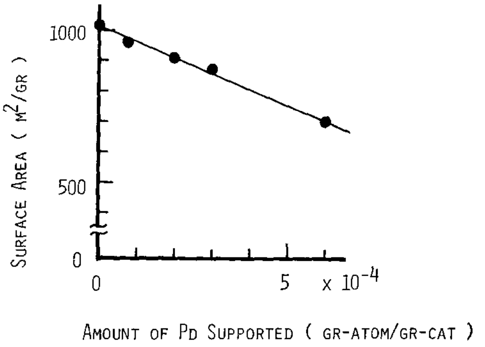


FIG. 13. Surface area of Pd–Te–C catalyst.

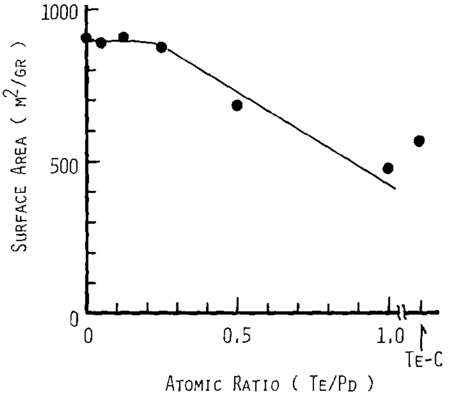
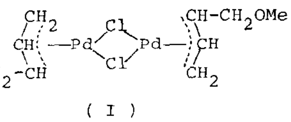


FIG. 14. Surface area of Pd–Te–C catalyst.

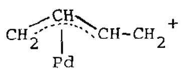
oxidation in liquid-phase is very slow (*15*). Moreover, Nakamura *et al.* (*16*) suggested that the catalytically active species is not Pd(OAc)$_2$ but dissociatively adsorbed acetic acid (Pd(I) acetate) on palladium in the gas-phase acetoxylation of ethylene. In the present work, as mentioned already, the solubilization of Pd into solvent was not clearly observed when the Pd–Te–C catalyst was used, and, therefore, the formation of Pd(OAc)$_2$ as the active species might not be agreeable because Pd(OAc)$_2$ may be easily soluble into acetic acid. The catalytic system of Pd–Te–C was suggested as a redox system consisting of a Pd–Te couple. No reaction was observed without oxygen (Fig. 5). Pd in the palladium tellurides is charged somewhat positively, but the highest activity was obtained with the catalyst containing Pd species of smaller positive charge, i.e., more metallic character (Fig. 10). Therefore, the active Pd species may be oxidized and subsequently activate acetic acid by the mechanism of its dissociative adsorption, being coupled with Te, in the presence of oxygen:

$$\mathrm{Pd} + \mathrm{AcOH} + \tfrac{1}{4}\mathrm{O_2} \rightarrow \mathrm{Pd}^{\oplus}\cdots\mathrm{OAc}^{\ominus} + \tfrac{1}{2}\mathrm{H_2O} \qquad (1)$$

The formation of DABs was observed at the beginning of the reaction and the amount of products other than 1,4-DABs and 3,4-DAB was negligible during the reaction (Fig. 8), implying that butadiene is directly acetoxylated to DABs on the active apecies. It has already been reported that metallic palladium works differently from palladium salt (e.g., PdCl$_2$) in the acetoxylation of olefins, i.e., the former gives the allylic derivatives and the latter gives vinylic ones (*17*). As for its mechanism, it was suggested that propylene, for example, is adsorbed in the form of a π-allyl type on Pd metal catalyst, contrary to the π-type on the Pd salt catalyst, the type of adsorbed intermediate depending uniquely on the strength of positive charge on palladium (*18*). In view of this, the active species in our catalysts seems to work rather with the metallic character, the π-allyl-type adsorption being preferred. Olefin has a hydrogen atom which can be abstracted as a hydride ion, giving a π-allyl complex; however butadiene has not such a hydrogen. Shaw *et al.* (*19, 20*) observed a π-allyl carbonium ion in binuclear complex of butadiene palladous chloride (I), which was conveniently prepared by passing

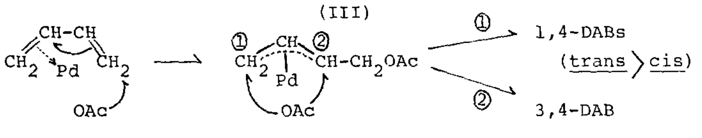


(I)

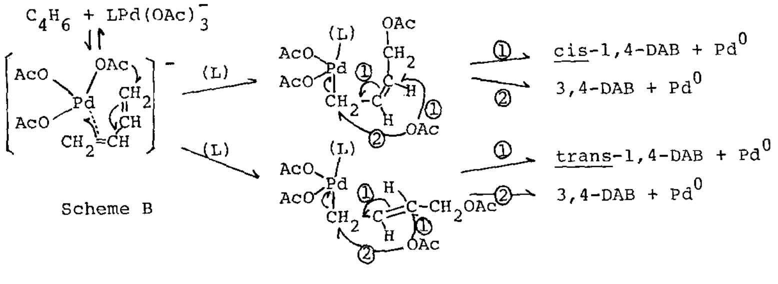


(II)

butadiene into a methanolic suspension of sodium chloropalladite. Allyl carbonium ions formed (II) may have considerable stability under the coexistence of counter-anion (*19*). Therefore, Scheme A, which proceeds via π-allyl intermediate (III), is considered. Butadiene molecule adsorbed on palladium which has weak positive charge undergoes acetoxylation on the terminal carbon atom, giving monoacetoxyl intermediate III. Intermediate III gives 1,4-DABs mainly and 3,4-DAB in proportion to the reactivity of carbon atom ① or ②. The distribution of *trans*- and *cis*-1,4-DABs is expected to be slightly affected by the reaction temperature. The result shown in Fig. 6, i.e., the small increment in *trans*-1,4-DAB selectivity observed at the expense of *cis*-1,4-DAB when the temperature was increased, gives support to this hypothesis. The parallel reactions from the intermediate III to 1,4-DABs and 3,4-DAB may be supported by the fact that the selectivity of products showed almost constant value during the reaction of 40 hr (Fig. 8).



Scheme A



Scheme B

The homogeneous metal acetates catalyst showed a relatively high activity for 1,4-diacetoxylation (Table 2, Expt 1 and Fig. 9); however, its selectivity for 1,4-DAB was low, being about 50%, accompanied by formations of 3,4-DAB and several unidentified products. When the reaction was carried out for 40 hr, small amount of palladium metal deposited on an inner wall of the reactor. The catalytic cycle may be the redox of Pd–Cu couple, and reaction Scheme B, based on analogies to other systems (*21*), is considered. The reaction seems to proceed via a π-complex, which is then converted into σ-complexes of *trans*- and *cis*-types by insertion of butadiene into Pd–OAc bond (or by attack of external OAc^- on the coordinated butadiene), and the obtained products consist mainly of 1,4-DABs and 3,4-DAB. Scheme B might possibly be applied to the reaction on the Pd–Te–C catalyst. However, it seems more reasonable to consider that the diacetoxylation proceeds via π-allyl intermediate (Scheme A) on the Pd–Te–C catalyst, because the higher activity of the catalyst was obtained when the smaller positive charge on its surface palladium was observed (Figs. 4 and 10), suggesting that Pd on the active species has a metal-like character.

When the $PdCl_2$ catalyst was used, the reaction rate was extremely low and a small amount of 3,4-DAB was detected together with some other unidentified products (Table 2, Expt 2). A similar result was obtained even when the reaction was carried out for 40 hr. The Pd–C catalyst prepared from $PdCl_2$, on which the XPS showed clearly the presence of $PdCl_2$ (Pd $3d_{5/2}$, 337.9 eV and Pd $3d_{3/2}$, 343.2 eV) (*11*) together with small amount of metallic palladium [Fig. 10, Pd–C (from $PdCl_2$)], served in a similar manner (Table 2, Expt 3). Pd on $PdCl_2$ has a large positive charge and may lead to a formation of the π-complex, from which monoacetoxy butadiene is formed as reported by Stern and Spector (*22*). Such a reaction results reasonably in the lowering of the 1,4-DAB selectivity. This unfavorable effect can also be observed somewhat when using catalysts prepared from $PdCl_2$ dissolved in hydrochloric acid (Table 2, Expts 3 to 10). Also when the metal acetates were used, the formation of such a π-complex cannot be completely denied, resulting in the low 1,4-DAB selectivity. Furthermore, it was reported that an isomerization of 3,4-DAB into 1,4-DAB (probably of *trans*-form) is catalyzed by Pd ions of higher valence at 150°C, Pd black showing contrarily no catalytic activity (*2*). Also in the present work, the metal acetates seem to have catalyzed somewhat the isomerization, while the Pd–Te–C catalyst, on which palladium is metallic, might not have strongly shown such an ability.

Thus, we have proposed the π-allyl-type intermediate mechanism (reaction Scheme A) for direct diacetoxylation of the butadiene on the Pd–Te–C catalyst. The reaction is summarized as follows:

$$CH_2{=}CH{-}CH{=}CH_2 + 2AcOH + \tfrac{1}{2}O_2 \xrightarrow{\text{Pd–Te–C}} \text{DAB } (\textit{trans}\text{-1,4-} > \textit{cis}\text{-1,4-} > \text{3,4-}) + H_2O$$

This is in good agreement with the fact that the ratio of the consumed butadiene and oxygen was about 2:1 during the reaction (Fig. 2).

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