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

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The catalytic properties of Rh–Te bimetallic system supported on charcoal (Rh–Te–C) for liquid-phase diacetoxylation of butadiene was studied in comparison with other heterogeneous [Pd–Te–C, Rh–(Se, Bi, or Sb)–C, Pt–Te–C, Ir–Te–C] or homogeneous [$Pd(OAc)_2$–$Cu(OAc)_2$–KOAc, $Pd(OAc)_2$–TeO_2–KOAc, etc.] noble metal-based catalysts. The Rh–Te–C catalyst prepared from $Rh(NO_3)_3$ and TeO_2 dissolved in aqueous nitric acid solution showed the highest activity of all the catalysts studied; its activity was about two times higher than that of Pd–Te–C. The reaction seems to proceed catalytically on the surface of this supported bimetallic system, though much of the Rh dissolves into the reaction media, and its active species is suggested to be a cationic Rh which acts by a redox mechanism, being coupled with Te. The use of the ratio of Rh : Te $\simeq$ 4 : 1 on charcoal is the most effective, which probably favors the formation of the cationic Rh species. The Rh–Te–C system catalyzed the direct diacetoxylation of butadiene, which is considered to proceed via cisoid conformation of butadiene followed by π-allyl type intermediate, resulting in the formation of *cis*-1,4-diacetoxy-2-butene as a main product. With the Rh–Te–C system, the following values of selectivities of diacetoxybutenes were obtained: *cis*-1,4-diacetoxy-2-butene, 87%, *trans*-1,4-diacetoxy-2-butene, 8%, and 3,4-diacetosy-1-butene, 5%.

I. INTRODUCTION

1,4-Butanediol is a useful industrial product as a comonomer for producing polybutylene terephthalate or as a raw material for making tetrahydrofurane, γ-butyrolactone, etc. For its industrial production, several processes have been proposed: oxidation of 1,3-butadiene followed by hydrogenation or hydroformylation of propylene derivatives such as allyl acetate, allyl alcohol, or acrolein (*1*). In the processes using 1,3-butadiene as the raw material, the most interesting one is hydrogenation followed by the hydrolysis of 1,4-diacetoxy-2-butene (1,4-DAB) prepared by the diacetoxylation of 1,3-butadiene; the 1,4-diacetoxylation is the key step in this process. Recently, many patents (*1*) have claimed the use of Wacker-type systems based on palladium as the catalyst for the 1,4-diacetoxylation, in which the most effective one appears to be the heterogeneous system: palladium coupled with tellurium and supported on charcoal (Pd–Te–C) (*2*); details have been previously reported by the authors (*3*). The Rh–Te–C system has been claimed in a few patents (*4*) to be more effective for 1,4-diacetoxylation than Pd–Te–C, though Rh is dissolved into the media during the reaction. However, no details of this catalyst system have been published except for the patent literature above. Here, we study the catalytic properties of Rh–Te–C systems in comparison with Pd–Te–C and other heterogeneous or homogeneous noble metal-based catalysts.

II. EXPERIMENTAL METHODS

1. Catalysts. The catalysts were prepared according to the previous report (*3*), i.e.,

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the noble metal (Rh, Pd, Pt, or Ir) salt was dissolved together with the oxide of the second component (Te, Se, Sb, or Bi) in water in the presence of 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 three kinds of charcoal (Takeda Shirasagi, surface area 845 m^2/g; Tsurumi HC42, surface area 800 m^2/g; Tsurumi HC30S, surface area 1166 m^2/g) pretreated with a 30% aqueous HNO_3 solution at 100°C for 6 hr. These supports were pulverized and used as 0.2- to 0.4-mm particle size powders. The metal salts used as homogeneous catalyst, such as palladium acetate ($Pd(OAc)_2$), rhodium acetate ($Rh_2(OAc)_4$), cupric acetate ($Cu(OAc)_2 \cdot H_2O$), etc, were used as received.

2. *Apparatus and procedure.* The oxidations were carried out using a gas-flow system. In a typical procedure, acetic acid and the catalyst were put into a 100-ml double-jacketed glass reactor equipped with a gas inlet and a condenser, and then the reaction mixture was heated at the requested temperature. After the temperature was reached, oxygen and butadiene at constant flow rates were bubbled into the reaction mixture.

Aliquot samples were then analyzed after the elimination of the catalyst by filtration.

3. *Analysis.* The oxidized products, *cis*-1,4-diacetoxy-2-butene (*cis*-1,4-DAB), *trans*-1,4-diacetoxy-2-butene (*trans*-1,4-DAB), and 3,4-diacetoxy-1-butene (3,4-DAB), were determined by gas chromatography using Shimadzu GC-7A fitted with a 3-m-long column Polyester FF 15% on Neosorb NS60/80. Monochlorobenzene was used as an internal standard. When the reaction did not proceed so sufficiently, the DABs were extracted with ethyl ether, and then were analyzed by gas chromatography after concentration in order to see their distributions.

The surface areas of the catalysts were measured by BET method using nitrogen. X-Ray photoelectron spectroscopy (XPS) was preformed by Shimadzu Multiple Surface Probe ASIX-1000 using monochromatic Al*Kα* radiation. All binding energy values were referenced to Cls (285.0 eV) (*3*). The distributions of Rh and Te in the catalyst particles were recorded on a Shimadzu electron probe X-ray microanalyzer (EMX), using Rh*Lα* and Te*Lα* lines. The samples were fixed on a sample holder with epoxy resin, then polished, and a thin Au film was plated on its surface by vacuum evaporation. The amount of dissolved Pd or Rh in the reaction solution was determined using the Shimadzu AA610S atomic absorption spectrophotometer.

III. RESULTS

1. Activity of Homogeneous Catalysts

Table 1 shows some representative results obtained with several homogeneous bimetallic systems. The Pd–Cu system (Run No. 1) showed the activity as already observed (*3*). The Pd–Te system gave a higher yield of DAB than the value estimated from stoichiometric reaction by Pd species (Run No. 2). Tellurium dioxide alone showed no activity. However, use of tellurium tetrachloride instead of tellurium dioxide in the Pd–Te system resulted in no activity. Rh systems did not show the catalytic activity (Run Nos. 3–5), and 2,3-and 2,4-DABs (Run Nos. 3 and 4) and an unidentified product (Run No. 5) were found together with 1,4- and 3,4-DABs in the samples extracted with ethyl ether. Heterogeneous Rh system catalysts showed, as shown later on, higher selectivity of *cis*-1,4-DAB, but the homogeneous Rh systems gave *trans*-1,4-DAB as a main product.

2. Activity of Heterogeneous Catalyst: Pd or Rh Coupled with Te

The representative results of the time

TABLE 1

Acetoxylation of Butadiene with Homogeneous Catalysts[a]

Catalyst system (mmol)	Reaction rate (mol-DAB/hr · g-atom Pd or Rh)	DAB						Reaction time (hr)	Run No.
		Yield (mmol)			Selectivity (%)				
		trans-1,4	*cis*-1,4	3,4	*trans*-1,4	*cis*-1,4	3,4		
$Pd(OAc)_2(0.5)Cu(OAc)_2(10)$ $-KOAc(25)$	4.41	7.66	0.69	0.81	83.6	7.5	8.8	5	1
$Pd(OAc)_2(0.5)TeO_2(5)$ $-KOAc(25)$	1.52	1.25	0.15	0.23	76.9	9.1	14.0	2	2
$Rh_2(OAc)_4(0.25)Cu(OAc)_2(10)$ $-KOAc(25)$	—	—	—	—	(86.0)[b]	(—)[b]	(14.0)[b]	5	3
$Rh_2(OAc)_4(0.25)TeO_2(5)$ $-KOAc(25)$	—	—	—	—	(84.8)[b]	(—)[b]	(15.2)[b]	2	4
$RhCl_3(0.5)CuCl_2(10)$ $-KOAc(25)$	—	—	—	—	(65.0)[c]	(3.9)[c]	(31.1)[c]	5	5

[a] Reaction temperature, 90°C; acetic acid, 50 ml; oxygen, 50 ml/min; butadiene, 50 ml/min.

[b] After the extraction with ethyl ether; 2,3- and 2,4-DABs were also detected.

[c] After the extraction with ethyl ether; an unidentified product was also detected.

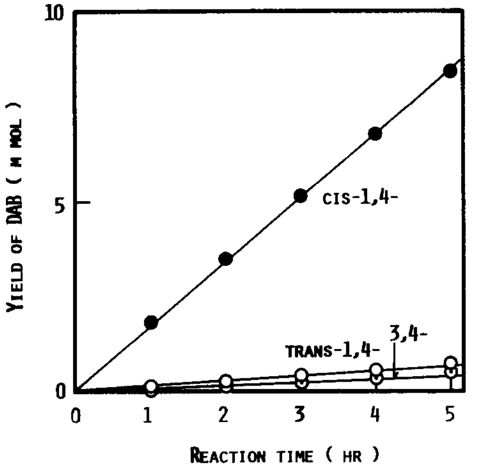


FIG. 1. Diacetoxylation with Rh–Te–C_{HC30S}. Reaction temperature, 90°C; catalyst, Rh–Te–C_{HC30S} (Rh, 0.1×10^{-3} g · atom/g-cat.; atomic ratio of Te/Rh, 1/4), 0.5 g; acetic acid, 50 ml; flow rate, butadiene, 50 ml/min; oxygen, 50 ml/min.

course of reaction with Rh–Te–C and Pd–Te–C catalysts are shown in Figs. 1 and 2. During the reaction for 5 hr, the activity of the catalyst was not lowered and its value is shown as the turnover number, i.e., the rate of DAB formation per 1 g-atom of noble metal per 1 hr.

Table 2 shows the results of oxidation with some heterogeneous catalyst. In the both cases with Pd–Te and Rh–Te couples, use of Tsurumi HC30S as a support resulted in the highest activity (Run Nos. 8 and 11), a part of which may be attributable to its large surface area. The main product with Pd–Te–C was *trans*-1,4-DAB, whereas *cis*-1,4-DAB was mainly obtained and the selectivity of 1,4-DAB reached the value of 95% with Rh–Te–C. The turnover number on Rh–Te–C was about 40 which is higher than the values found in the patent literatures (*1*, *4*). However, a large amount of Rh was dissolved in the reaction media (Run Nos. 9–11), though Pd was not detected by the atomic absorption measurement (Run Nos. 6–8). As the cocatalyst, Te was most effective, followed by Se, and both Sb and Bi showed almost no effect (Run Nos. 11–14). The distribution of the products was somewhat affected by the nature of cocatalyst. A large amount of Rh dissolved into the media from a much more active catalyst. It is noteworthy that the Rh system works only as a heterogeneous system, though the Pd system is active as both heterogeneous and homogeneous systems (Tables 1 and 2).

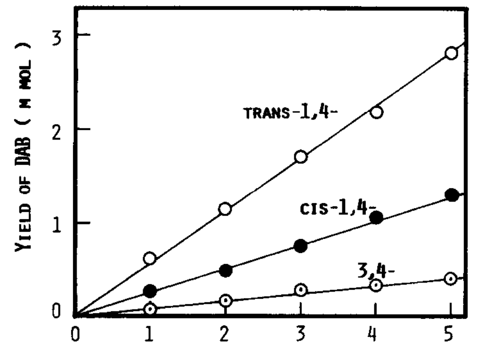


FIG. 2. Diacetoxylation with Pd–Te–C_{HC30S}. Reaction temperature, 90°C; catalyst, Pd–Te–C_{HC30S} (Pd, 0.1×10^{-3} g · atom/g-cat.; atomic ratio of Te/Pd, 1/4), 0.5 g; acetic acid, 50 ml/min; flow rate, butadiene, 50 ml/min; oxygen, 50 ml/min.

3. *Behaviors of Rh–Te–C Catalyst*

Figure 3 shows the dependence of the activity on the atomic ratio of Te : Rh. When

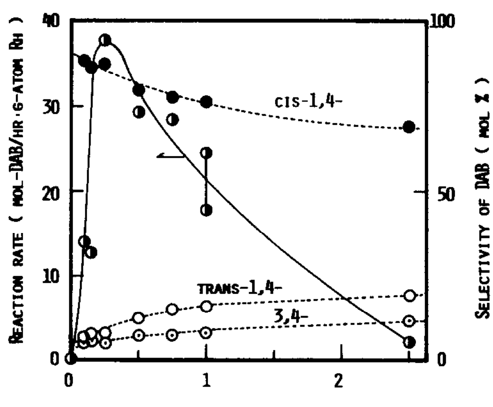


FIG. 3. Effect of the addition of tellurium. Reaction temperature, 90°C; reaction time, 5 hr; catalyst, Rh–Te–C_{HC30S} (Rh, 0.1×10^{-3} g · atom/g-cat.), 0.5 g; acetic acid, 50 ml; flow rate, butadiene, 50 ml/min; oxygen, 50 ml/min.

TABLE 2

Acetoxylation of Butadiene with Heterogeneous Catalysts[a]

Catalyst	Composition (atomic ratio)	Surface area (m^2/g)	Reaction rate (mol DAB/hr·g-atom Pd or Rh)	DAB						Amount of Pd or Rh dissolved (10^{-6} g-atom)	Run No.
				Yield (mmol)			Selectivity (%)				
				trans-1,4	*cis*-1,4	3,4	*trans*-1,4	*cis*-1,4	3,4		
Pd-Te-$C_{shirasagi}$	Pd/Te = 4/1	388	16.0	2.79	1.63	0.41	57.7	33.7	8.5	n.d.	6
Pd-Te-C_{HC42}	Pd/Te = 4/1	506	14.9	2.80	1.31	0.41	62.0	28.9	9.0	n.d.	7
Pd-Te-C_{HC30S}	Pd/Te = 4/1	681	17.3	3.10	1.61	0.48	59.7	31.1	9.2	n.d.	8
Rh-Te-$C_{shirasagi}$	Rh/Te = 4/1	691	12.1	0.34	2.48	0.27	11.0	80.4	8.5	2.43	9
Rh-Te-C_{HC42}	Rh/Te = 4/1	623	29.9	0.63	6.55	0.45	8.3	85.8	5.9	2.77	10
Rh-Te-C_{HC30S}	Rh/Te = 4/1	835	37.8	0.76	8.41	0.50	7.8	87.0	5.1	2.87	11
Rh-Se-C_{HC30S}	Rh/Se = 4/1	610	7.2	0.49	1.14	0.22	26.4	61.8	11.7	1.02	12
Rh-Sb-C_{HC30S}	Rh/Sb = 4/1	637	—	—	—	—	(7.6)[b]	(18.8)[b]	(13.6)[b]	0.25	13
Rh-Bi-C_{HC30S}	Rh/Bi = 4/1	749	—	—	—	—	(21.6)[b]	(47.4)[b]	(31.0)[b]	0.78	14

[a] Reaction temperature, 90°C; reaction time, 5 hr; acetic acid, 50 ml; catalyst, 0.5 g; oxygen, 50 ml/min; butadiene, 50 ml/min. The catalyst was prepared from $Pd(NO_3)_2$ or $Rh(NO_3)_3$ and the oxide of second component dissolved in HNO_3 aq. soln.; concentration of metal, Pd or Rh, 0.12 mg-atom/g-cat.

[b] After the extraction with ethyl ether.

no Te is added, a very low activity is observed. However, the addition of a small amount of Te to the Rh–$\mathrm{C_{HC30S}}$ catalyst results in a dramatic increase in activity. The activity reached a maximum at a ratio Rh : Te ≃ 4 : 1, and a further increase of the ratio caused the decrease of the activity. The selectivity of DAB was somewhat affected by the atomic ratio, that is, *trans*-1,4- and 3,4-DABs increased at the expense of *cis*-1,4-DAB.

Figure 4 shows the amount of Rh dissolved after the reaction mentioned above. Its dependence on the atomic ratio may well coincide with that of the activity (Fig. 3), when taking account of the surface area of the catalyst shown in Fig. 5. That is, a large amount of Rh dissolved from the catalyst showing a high specific activity. The amount of Rh dissolved reached a maximum value of 4.9 × 10^{-6} g · atom, corresponding to 9.4% of total Rh supported, at the atomic ratio of Rh : Te = 2 : 1. It was confirmed that acetic acid can dissolve a similar amount of Rh after suspending the catalyst in it at 90°C for 5 hr. Here, homogeneous catalytic oxidation by such a dissolved Rh species may be considered. However, this possibility was denied by two experimental results; 0.5 g of Rh–Te–$\mathrm{C_{HC30S}}$ (Rh: 0.1 × 10^{-3} g · atom/g-cat., Rh : Te = 4 : 1) was suspended in 50 ml of acetic acid at 90°C for 5 hr, then solid catalyst separated by filtration, and the acetic acid solution (dissolved Rh: 2.58 × 10^{-6} g · atom/50 ml) was used for the reaction under the flow rate of butadiene: 50 ml/min and oxygen: 50 ml/min for 5 hr at 90°C, with no formation of DABs. Another experiment was done as follows: in the presence of the same catalyst as above, the reaction was carried out for 5 hr under the same condition as Run No. 11. After the elimination of solid catalyst, the acetic acid solution containing *cis*-1,4-DAB, 8.35 mmol, *trans*-1,4-DAB, 0.80 mmol, 3,4-DAB, 0.45 mmol, and the dissolved Rh, 2.95 × 10^{-6} g · atom was employed for the same reaction as above, resulting in no change in the amount of each DABs. Thus, it was suggested that Rh–Te–$\mathrm{C_{HC30S}}$ works as a heterogeneous catalyst, though much Rh dissolves into the reaction medium from the catalyst.

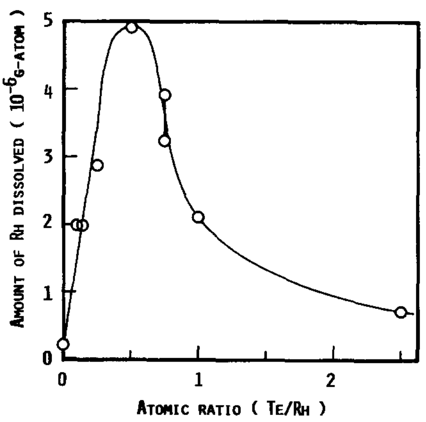


Fig. 4. Amount of Rh dissolved. Reaction temperature, 90°C; reaction time, 5 hr; catalyst, Rh–Te–$\mathrm{C_{HC30S}}$ (Rh, 0.1 × 10^{-3} g · atom/g-cat.), 0.5 g; acetic acid, 50 ml; flow rate, butadiene, 50 ml/min; oxygen, 50 ml/min.

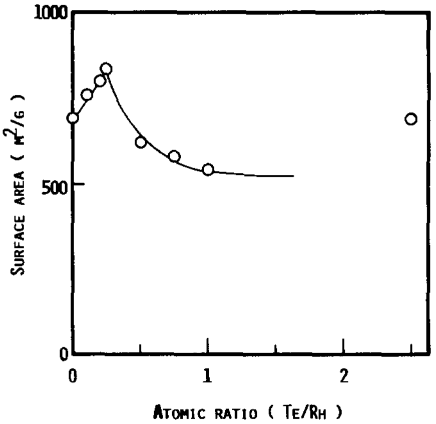


Fig. 5. Surface area of Rh–Te–$\mathrm{C_{HC30S}}$ catalyst. Rh, 0.1 × 10^{-3} g · atom/g-cat.

Figure 6 shows the influence of the amount of metal on the activity of the catalyst. The turnover number increased by increasing the amount of Rh and Te supported on charcoal at a ratio Rh : Te = 4 : 1 until a concentration of 0.1–0.2 × 10^{-3} g · atom Rh/g-cat. is reached. However, a further addition of the metals caused a de-

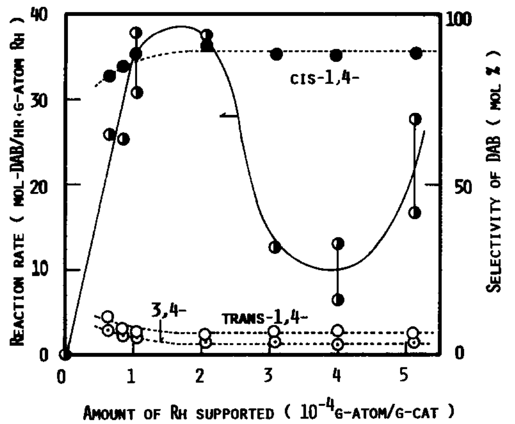


FIG. 6. Effect of metal concentration on catalyst. Reaction temperature, 90°C; reaction time, 5 hr; catalyst, Rh–Te–C_{HC30S} (atomic ratio of Te/Rh, 1/4), 0.5 g; acetic acid, 50 ml; flow rate, butadiene, 50 ml/min; oxygen, 50 ml/min.

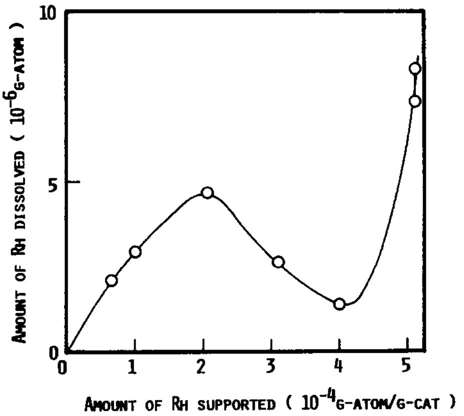


FIG. 7. Amount of Rh dissolved. Reaction temperature, 90°C; reaction time, 5 hr; catalyst, Rh–Te–C_{HC30S} (atomic ratio of Te/Rh, 1/4), 0.5 g; acetic acid, 50 ml; flow rate, butadiene, 50 ml/min; oxygen, 50 ml/min.

crease of the turnover number, which may be attributable partly to a lowering of the surface area of the catalyst as shown in Fig. 8. The lowering of the surface area may be due to the filling of micropores in charcoal with the metals, as shown later on in the results of EMX analysis (Fig. 10). The amount of Rh dissolved (Fig. 7) showed a similar relationship to the activity, that is, a large amount of Rh dissolved from the active catalyst. The highest value of about 8×10^{-6} g · atom Rh observed at 0.5×10^{-3} g · atom Rh/g-cat. suggests that the active Rh species begins to cover the catalyst surface by forming a thick layer when the amount of Rh supported is over such a value. The solution after the impregnation, when preparing the catalyst containing Rh below 0.4×10^{-3} g · atom/g-cat., was colorless and transparent, but brown in the case of Rh content: 0.5×10^{-3} g · atom/g-cat., which shows that an excess amount of metals remained in the solution after reaching the adsorption equilibrium in the latter case. Such excess metals may deposit on the surface of the catalyst particle after the evaporation of water *in vacuo*. The details will be shown later in the results of EMX analysis.

4. Kinetics of the Reaction

The effect of partial pressures were studied by changing the gas-phase composition. The results are shown in Fig. 9. There was no oxidation observed without oxygen, and the reaction order with respect to both oxygen and butadiene calculated from the reaction rate was about 1.0. The higher rate observed under the higher concentration of oxygen may be due to its lower solubility

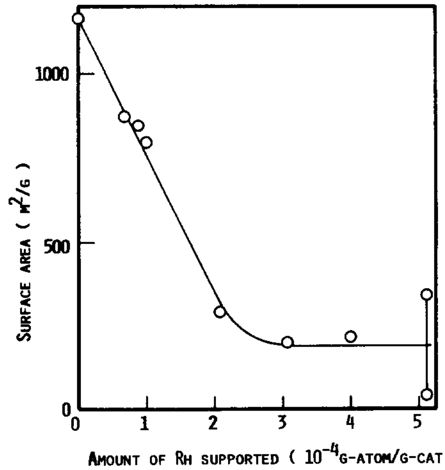


FIG. 8. Surface area of Rh–Te–C_{HC30S} catalyst. Atomic ratio of Te/Rh, 1/4.

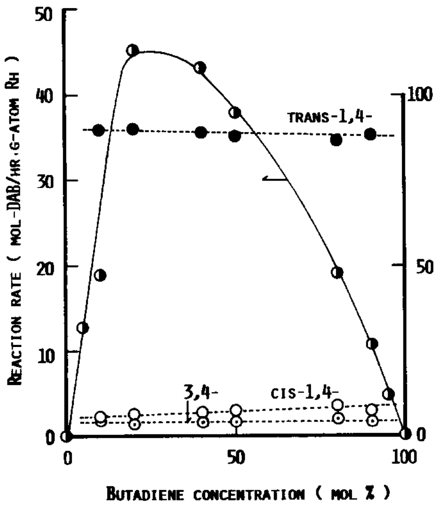


FIG. 9. Effect of composition in gas-phase. Reaction temperature, 90°C; catalyst, Rh–Te–C_{HC30S} (Rh, 0.1 × 10^{-3} g · atom/g-cat., atomic ratio of Te/Rh = 1/4), 0.5 g; acetic acid, 50 ml; flow rate of butadiene and oxygen, 100 ml/min; reaction time, 2 hr.

than butadiene in acetic acid. The reaction order with respect to the catalyst was 0.82. An apparent activation energy obtained by changing the reaction temperature from 60 to 90°C was about 8.2 kcal/mol.

5. *Properties of the Catalyst*

Two representative results of metal distributions in the catalyst particles obtained by EMX measurements are shown in Fig. 10. In most of the catalyst used, Rh and Te were detected even in the cores, to say nothing of the surface layers, though their concentrations decreased somewhat on going toward the interior of the particles. It is suggested that a main part of the metals was used for filling the micropores in the catalyst particle. When increasing the amount of the metals over the value of 0.5 × 10^{-3} g · atom Rh/g-cat., a large amount of the metals was observed in the surface layers of the catalyst particles; such a particle is covered with a thick layer of the metals. The two metals were observed to distribute at an approximately constant ratio of Te : Rh 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 similarly to the case of Pd–Te–C catalyst (*3*).

The surface properties of the Rh–Te–C catalyst prepared from $Rh(NO_3)_3$ and TeO_2 dissolved in aqueous nitric acid solution were studied by XPS. The results are shown in Figs. 11 and 12. The binding energies (B.E.) of $RhCl_3$ as a reference were as follows: Rh 3d5/2, 310.5 eV; Rh 3d3/2, 315.3 eV; these values are quite close to the literature data (*5*). TeO_2 showed a slightly lower value of B.E. (Te 3d5/2, 575.3 eV) than 575.9–576.2 eV shown in the literature (*6–8*). Rh on the Rh–C_{HC30S} catalyst (Rh: 0.1 × 10^{-3} g · atom/g-cat.) containing no Te seems to be mainly in the Rh(0) state (Rh 3d5/2, 307.5 eV), though this value is higher by 0.2–0.5 eV than that for bulk Rh metal (307.0–307.3 eV) (*5, 9, 10*). This finding is considered to reflect the particle size of the Rh metal, taking into account the effect of an electron transfer from the metal to the

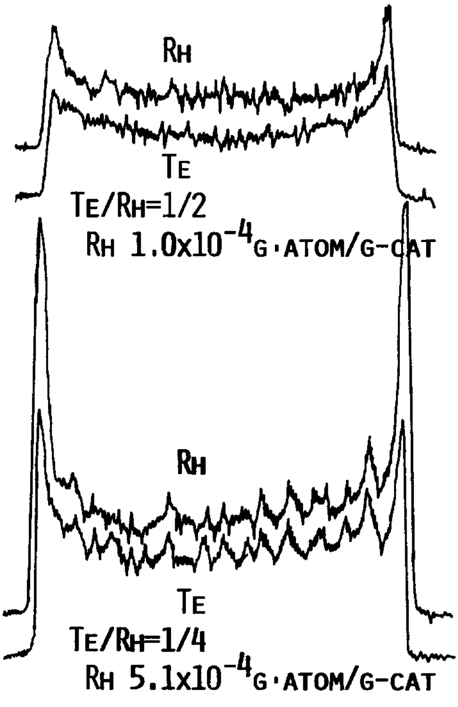


FIG. 10. EMX of Rh–Te–C_{HC30S} catalyst particle.

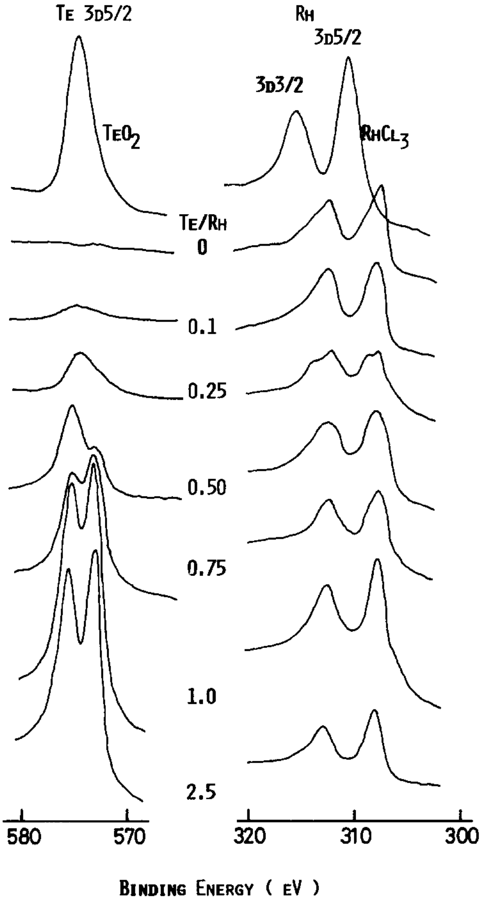


Fig. 11. Photoelectron spectra of Rh 3d and Te 3d on catalyst surface.

charcoal as observed in the Rh-zeolite catalyst (*5*); the smaller the metal particle, the larger is the expected effect due to electron transfer. When adding a small amount of Te to the Rh–$\mathrm{C_{HC30S}}$ catalyst, the B.E. shifted toward a slightly higher value of Rh 3d5/2: 307.8 eV (Te/Rh = 1/10); a further increase of Te resulted in the appearance of an additional peak at 308.8 eV (Te/Rh = 1/4). The catalysts containing more Te showed the value of Rh 3d5/2: 307.8 eV. As for the energy level of Te 3d5/2, the following results were obtained. The catalysts of low Te/Rh ratio (1/10 and 1/4) mainly showed the signal of Te 3d5/2: 574.4 eV which is lower than 575.3 eV of $\mathrm{TeO_2}$. On increasing this ratio, two signals, i.e., 575.0–575.2 and 572.7–573.0 eV, appeared and the intensity of the latter became stronger. The former and the latter signals can be assigned to $\mathrm{TeO_2}$ (Te 3d5/2: 575.3 eV) and Te(0) (Te 3d5/2: 572.7–571.1 eV) (*6, 7, 11*), respectively. The possibility cannot be denied that the signal of Te 3d5/2: 574.4eV exists in the spectra of the catalysts of higher Te/Rh ratio than 1/2. When the amount of the metals was increased at the constant ratio of Te/Rh: 1/4 (Fig. 12), the intensities of both the signals of Rh and Te were enhanced and the latter was split into two signals: one (Te 3d5/2: 575.0–575.1 eV) being assigned to $\mathrm{TeO_2}$ and another (Te 3d5/2: 573.1–573.3 eV) to Te(0). The signal of Rh 3d5/2 observed at 308.8 eV on the catalyst containing 0.1×10^{-3} g · atom Rh/g-cat. was not so clear on the catalysts of higher metals content. All the B.E. values of Rh 3d5/2 on catalysts of Rh–Se–$\mathrm{C_{HC30S}}$, Rh–Bi–$\mathrm{C_{HC30S}}$, and Rh–Sb–$\mathrm{C_{HC30S}}$ were nearly 307.8 eV.

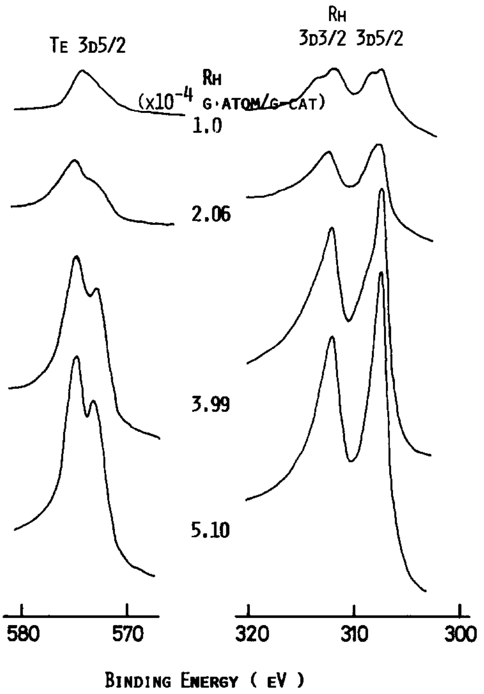


Fig. 12. Photoelectron spectra of Rh 3d and Te 3d on catalyst surface.

TABLE 3

Acetoxylation of Butadiene with Heterogeneous Catalysts[a]

Catalyst	Raw materials	Surface area (m^2/g)	Reaction rate (mol DAB/hr·g-atom Rh or Pd)	DAB						Amount of Pd or Rh dissolved (10^{-6} g-atom)	Run No.
				Yield (mmol)			Selectivity (%)				
				trans-1,4	*cis*-1,4	3,4	*trans*-1,4	*cis*-1,4	3,4		
Pd–Te–C_{HC30S}	$PdCl_2$, TeO_2[b]	1029	13.6	1.85	0.64	0.23	67.9	23.8	8.3	n.d.	15
Rh–Te–C_{HC30S}	$RhCl_3 \cdot 3H_2O$, TeO_2[b]	1129	14.6	0.43	2.30	0.19	14.8	78.6	6.6	2.52	16
Pt–Te–C_{HC30S}	$H_2PtCl_6 \cdot 6H_2O$, TeO_2[b]	1076	5.1	0.64	0.20	0.19	62.2	19.3	18.5		17
Ir–Te–C_{HC30S}	$IrCl_4$, TeO_2[b]	477	1.0	Trace	0.19	Trace	14.3	76.6	9.1		18
Rh–Te–C_{HC30S}	$RhCl_3 \cdot 3H_2O$, TeO_2[c]	875	16.0	0.30	2.65	0.25	9.4	82.9	7.7	2.43	19
Rh–Te–C_{HC30S}	$Rh(NO_3)_3$, TeO_2[c]	842	35.5	0.54	5.93	0.33	8.0	87.2	4.8	1.74	20
Pd–Te–C_{HC30S}	$PdCl_2$, TeO_2[c]	953	10.0	1.18	0.65	0.17	59.3	32.3	8.3	n.d.	21

[a] Reaction temperature, 90°C; reaction time, 2 hr; acetic acid, 50 ml; catalyst, 1.0 g; oxygen, 50 ml/min; butadiene, 50 ml/min; concentration of metal in the catalyst: Pd, Rh, Pt, or Ir, 0.1 mg-atom/g-cat.; Te, 0.025 mg-atom/g-cat.

[b] The raw materials were dissolved in HCl aq. soln.

[c] The raw materials were dissolved in HNO_3 aq. soln.

6. Influence of the Nature of the Catalyst System

The results obtained by replacing Rh with another metal, Pd, Pt, or Ir, are shown in Table 3. Metal chlorides as the raw materials were chosen in order to obtain a good dissolution in HCl aqueous solution in the catalyst preparation (Run Nos. 15–18), and therefore their activities are not as high as in the case of using metal nitrate (*vide infra*). The activity can be put in the following order: Rh–Te–C_{HC30S} > Pd–Te–C_{HC30S} > Pt–Te–C_{HC30S} > Ir–Te–C_{HC30S}. Concerning the product selectivity, Pd and Pt systems gave a high amount of *trans*-1,4-DAB and Rh and Ir systems mainly gave *cis*-1,4-DAB. Pd–Te–C_{HC30S} showed no solution of Pd; however some Rh dissolved from Rh–Te–C_{HC30S}.

Use of $Rh(NO_3)_3$ instead of $RhCl_3$ and nitric acid instead of hydrochloric acid as the solvent for the preparation of Rh–Te–C_{HC30S} catalyst results in higher activity for the 1,4-diacetoxylation of butadiene and also in less solution of Rh in the reaction solution (Run Nos. 16, 19, and 20). According to the analytical results by XPS, the Rh–Te–C_{HC30S} catalyst prepared with the chloride showed the weak signals of Cl 2sl/2 (270 eV) and Cl 2p3/2 (200 eV), and the signal of Rh 3d5/2 (307.7 eV) broadened toward a higher energy state, suggesting that chlorine remains and combines with rhodium on the catalyst surface. Such a rhodium species may reasonably have higher oxidation states than metallic rhodium.

Table 4 shows the effect of the addition of potassium acetate or acetic anhydride in the reaction with the Rh–Te–C_{HC30S} (Te/Rh = 1/4, Rh: 0.1×10^{-3} g · atom/g-cat.) catalyst. Potassium acetate is expected to react as an acetoxylating agent by dissociating into potassium cation and acetoxy anion on the catalyst surface, but the result did not show such a favorable effect. Acetic anhydride is known to work as a dehydrating agent and showed no increment in the activity. In both cases, a decrease in the solution of Rh was accompanied by a decrease of the activity.

TABLE 4

Effect of the Addition of Potassium Acetate or Acetic Anhydride[a]

Substance added (mmol)	Amount of Rh dissolved (10^{-6} g-atom)	Reaction rate (mol DAB/hr g-atom Rh)
None	1.35	36.5
KOAc (25)	0.68	17.6
Ac_2O (52.2)	0.97	14.8

[a] Catalyst used, Rh–Te–C_{HC30S} (Te/Rh = 1/4, Rh 0.1 mg-atom/g-cat.), 0.5 g; acetic acid, 50 ml; butadiene, 50 ml/min; oxygen, 50 ml/min. Reaction temperature, 90°C; reaction time, 2 hr.

IV. DISCUSSION

According to the results obtained in the previous paper (*3*), it was suggested that Pd works as a diacetoxylation catalyst by a redox mechanism, being coupled with Te, in which Te serves as a reoxidizing agent of reduced Pd species on the heterogeneous Pd–Te–C catalyst. The result obtained in the homogeneous Pd–Te coupled system (Run No. 2) supports this mechanism, because tellurium dioxide alone showed no activity. No activity observed in the use of tellurium tetrachloride instead of tellurium dioxide suggests the importance of the Te–O bond in the catalytic system of Pd–Te couple, but details are not clear.

$RhCl_3$–$CuCl_2$ catalyst was used in the oxidation of ethylene to acetaldehyde in aqueous hydrochloric acid solution (*12, 13*). James *et al.* (*12*) have indicated that the oxidation is catalyzed by the redox of Rh(III)–Rh(I) cycle in the presence of an excess of an oxidizing agent of Cu(II)/oxygen system similar to the well-known Wacker process which employs a Pd–Cu couple, but the Rh(I) species are labile and easily converted into Rh(II) and metallic Rh by the disproportionation reaction. Osipov *et al.* (*13*) have briefly mentioned the use of acid chloride solutions containing $RhCl_6^{3-}$, and noted that the activity was some 150 times less than that of $PdCl_4^{2-}$ solutions under the same conditions (90°C, < 1 atm pressure and using Cu(II)/oxygen to regenerate the catalyst). Our results obtained by using a homogeneous Pd or Rh system catalyst (Table 1) are in good accord with such observations; Rh systems showed very low activity comparing to Pd systems.

The activity of the heterogeneous Rh system catalysts can be put in the following order: Rh–Te–C_{HC30S} > Rh–Se–C_{HC30S} > Rh–Sb–C_{HC30S} ≃ Rh–Bi–C_{HC30S}, which agrees well with that observed previously with the Pd system catalyst in the viewpoint of the effect of cocatalyst related to the oxidation potential (*3*). This indicates that the oxidation on the heterogeneous catalysts proceeds by a mechanism of Rh redox coupled with Te or Se as a reoxidizing agent, as already mentioned in the case of homogeneous $Pd(OAc)_2$–TeO_2 couple.

When changing the atomic ratio of Te/Rh, the highest activity of the Rh–Te–C_{HC30S} catalyst was obtained at the ratio of 1/4 ~ 1/2 (Fig. 3). These catalysts showed the additional peak of Rh 3d5/2 at 308.8 eV together with the peak of Rh 3d5/2 at 307.8 eV attributable to Rh(0) species in the XPS spectra (Fig. 11). The value of B.E. of the former Rh 3d5/2 peak is near to those of $Rh_2(OAc)_4$ (Rh 3d5/2 306.2 eV) (*14*) and Rh_2O_3 (Rh 3d5/2 309.1 or 308.4 eV) (*10, 15*). When considering the redox system between Rh(III) and Rh(I) as already noted in the oxidation of ethylene to acetaldehyde, it seems probable that the former peak is assigned to Rh(I) species, though its details are not clear. It can be considered that this cationic Rh(I) species is formed by the interaction between Rh and Te, similarly to the case of Pd–Te–C catalyst (*3*). However, it should be noticed that the active species on the Pd–Te–C catalyst is a metallic Pd which keeps a weak positive charge, and its catalytic redox system is recycled between Pd(II) and Pd(O). In the present case of the Rh–Te–C_{CH30S} catalyst, the active species may be the cationic Rh(I) species. It may be reasonable that such a cationic Rh(I) species is more easily dissolved into acetic acid than the metallic Rh(0) species. This consideration agrees very well with the results in Fig. 4. The decrease of the catalytic activity when increasing the Te/Rh ratio over 1/2 can be due to both the decrease of the cationic Rh(I) species and the covering of the catalyst surface by the inactive Te species as already noted. The homogeneous Rh species did not catalyze the reaction; the heterogeneous mechanism was suggested. It also seems possible that transient Rh(I) species are produced from the catalyst surface, catalyze the desired reaction, and are finally lost as inactive Rh(III) or other species into solution, i.e, quasi-heterogeneous mechanism. In the latter case, the catalyst works as the reservoir of the active Rh(I) species. In the present study, we cannot decide which of the true and the quasi-heterogeneous mechanisms should be adopted.

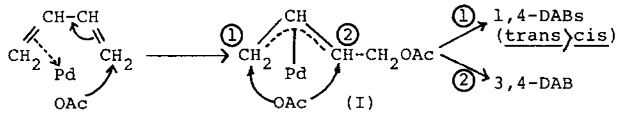
The dependence of the catalytic activity on the amount of metals supported (Fig. 6) can be explained as follows: the Rh–Te–C_{HC30S} catalysts of Rh content of 1.0 ~ 2.0 × 10^{-4} g · atom/g-cat. may contain the cationic Rh(I) species on the surfaces according to XPS analysis (Fig. 12) and showed higher activities. A further increase in the metals content resulted in lowering of the activity which may be due to the decrease of the amount of the active species.

The activity increment observed at a much higher content of Rh is presumably due to the presence of the cationic active species in the surface skin of the metals deposited on the catalyst as already noted because of a highly enhanced solution of Rh.

Replacing Rh by Pd, Pt, or Ir resulted in the following order of the catalytic activity: Rh–Te–C_{HC30S} > Pd–Te–C_{HC30S} > Pt–Te–C_{HC30S} > Ir–Te–C_{HC30S}, which is in fairly good agreement with the order of the oxidation potential: Rh/Rh^{3+}, 0.80 V < Pd/Pd^{2+}, 0.987 V < Ir/Ir^{3+}, 1.156 V < Pt/Pt^{2+}, 1.2 V (*16*). Though the latter order should be modified because it seems probable that the catalytic redox system is composed of Rh^+/Rh^{3+} and Ir^+/Ir^{3+} cycles, this agreement may support the redox mechanism of the metals coupled with Te in the catalytic system. On considering the relatively low value of the oxidation potential of Te/Te^{4+}, 0.529 V, the metal of lower oxidation potential can favorably form the redox system coupled with Te, resulting in higher activity.

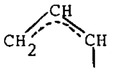
The enhanced solution of Rh in spite of the lower activity, observed with the catalyst of higher chlorine content (Run Nos. 16, 19, and 20), is reasonably due to the formation of rhodium chloride compounds on the surface. The presence of chlorine may cause either the higher valence states of Rh, unfavorable for the activation of butadiene by its π-allyl adsorption on Rh (*vide infra*), or the hindrance for the electron transfer between Rh and Te. It seems reasonable that the rhodium chlorides are easily dissolved into the reaction media.

The authors have previously proposed the π-allyl intermediate mechanism for the diacetoxylation of butadiene on the Pd–Te–C catalyst (*3*); the butadiene molecule adsorbed on Pd which has a weak positive charge undergoes acetoxylation on the terminal carbon atom, giving a monoacetoxyl intermediate of the π-allyl type (I).

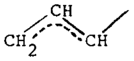


(1)

A π-allyl complex with a substituent will be capable of existence in *syn-* and *anti*-conformations, which, when viewed normal to the surface, will appear as:

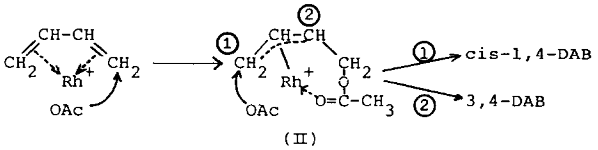


anti-



syn-

Free rotation between these conformers is prohibited (*17*). The π-allyl intermediate (I) with the bulky substituent seems to exist exclusively as the *syn*-conformer (*18*). This is because the thermodynamic stability of the complex in this conformation is higher than in the *anti*-conformation on account of the lower steric hindrance between the substituent and the metal atom. Therefore, the formation of *trans*-1,4-DAB as the main product can be explained by the π-allyl intermediate mechanism. In the present reaction on the Rh–Te–$\mathrm{C_{HC30S}}$ catalyst, however, the main product was *cis*-1,4-DAB which is hardly formed from the π-allyl type intermediate in the *syn*-conformation. In the cases known so far, butadiene is coordinated as a bidentate group to cationic Rh species, i.e., in the cisoid conformation (*19*). The following scheme is considered as a main route in the diacetoxylation of butadiene on the Rh–Te–$\mathrm{C_{HC30S}}$ catalyst:



(2)

Butadiene adsorbed in the cisoid form on the cationic Rh species may keep the same conformation, i.e., the π-allyl intermediate (**II**), by donating lone pair electrons on a carbonyl oxygen atom to the cationic metal after the monacetoxylation. The formation of small amount of *trans*-1,4-DAB suggests reaction (1) as the side reaction on the Rh–Te–C_{HC30S} catalyst. Some π-allyl complexes of butadiene have been observed on the cationic Rh species (*20*).

When coupled with Te, Pd and Pt gave *trans*-1,4-DAB as the main product, and Rh and Ir gave *cis*-1,4-DAB. The former metals may work in the metallic state, the latter in the cationic state, when considering the redox cycles of Pd–Pd^{2+}, Pt–Pt^{2+}, Rh^{+}–Rh^{3+}, and Ir^{+}–Ir^{3+}. It seems probable that the metallic and cationic species mainly catalyze the paths of the π-allyl intermediates (**I**) and (**II**), respectively.

Acetoxylation of monoacetoxybutene was carried out in order to verify the π-allyl intermediate mechanism. 4-Acetoxy-1-butene or 4-acetoxy-2-butene was oxidized in acetic acid in the presence of Rh–Te–C_{HC30S} or Pd–Te–C_{HC30S} catalyst under oxygen flow. Some representative results are shown in Table 5. 4-Acetoxy-1-butene was oxidized far more slowly than butadiene and showed a similar distribution of products to that of the butadiene oxidation on each binary metal catalyst. The oxidation of 4-acetoxy-2-butene gave similar results; a main product was 1,4-DABs, in which *trans*-isomer was mainly obtained on Pd, *cis*-isomer on Rh. It seems probable that each monoacetoxy-butene can be adsorbed in π-allyl form after hydrogen abstraction on the Pd–Te or Rh–Te system catalyst, and hence, the similarity of the product distributions observed in the oxidations of butadiene and the monoacetoxybutenes may lead us to the validity of the π-allyl intermediate mechanism. Use of 1-butene instead of butadiene with these catalysts under the condition shown in Table 2 resulted in a very low rate of reaction and a product distribution which is similar to the case of the monoacetoxybutene oxidation. This suggests a low ability of these catalysts for hydrogen abstraction, considering that 1-butene can be oxidized passing through a hydrogen abstraction step. The lower reactivity of the monoacetoxybutenes compared with butadiene can be explained by this lower ability to hydrogen abstraction of the Pd–Te or Ph–Te system catalysts.

Thus, we have proposed the cationic Rh species as the active site, and the π-allyl intermediate mechanism (**II**) as the main reaction in the direct diacetoxylation of butadiene on the Rh–Te–C catalyst. These can well explain the solution of Rh during the reaction and the product distribution.

TABLE 5

Acetoxylation of 4-Acetoxy-1-butene[a]

Catalyst	Reaction rate (mol DAB/hr·g-atom Pd or Rh)	Selectivity (%)		
		trans-1,4	*cis*-1,4	3,4
Pd–Te–C_{HC30S}[b]	0.37	67.4	21.8	10.8
Rh–Te–C_{HC30S}[c]	0.14	10.6	78.0	11.4

[a] Reaction temperature, 90°C; reaction time, 2 hr; acetic acid, 50 ml; 4-acetoxy-1-butene, 0.4 ml; catalyst, 0.5 g; oxygen, 70 ml/min.

[b] Prepared from $PdCl_2$ and TeO_2 in HCl aq. soln.; Pd, 0.1 mg-atom/g-cat.; Te/Pd = 1/4; surface area, 953 m^2/g.

[c] Prepared from $Rh(NO_3)_3$ and TeO_2 in HNO_3 aq. soln.; Rh, 0.1 mg-atom/g-cat.; Te/Rh = 1/2; surface area, 621 m^2/g.

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