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Liquid-Phase Oxidative Lactonization of Butane-1,4-diol into γ-Butyrolactone with Oxygen over Palladium Supported on K-L Zeolite

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Synopsis. Pd^0 supported on K-L zeolite suspended in a liquid phase has a high catalytic activity and a high selectivity for the oxidative lactonization of butane-1,4-diol into γ-butyrolactone under oxygen at 391 K.

Many methods for the preparation of lactones by the homogeneous metal-catalyzed oxidative lactonization of such α,ω-diols as butane-1,4-diol have been reported.[1–4] Homogeneous catalysts such as palladium acetate ($Pd(OAc)_2$)[1] catalyze the oxidative lactonization of α,ω-diols in the presence of such oxidants as a stoichiometric amount of bromobenzene (PhBr) and an excess of triphenylphosphine (Ph_3P) in order to oxidize the Pd^0 and generate the active species **1** as follows:

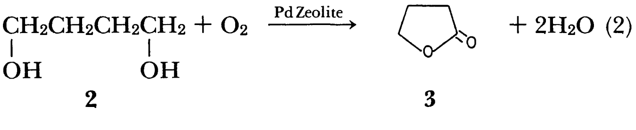
$$Pd^0(Ph_3P)_n + PhBr \longrightarrow \underset{\mathbf{1}}{PhPd(Br)(Ph_3P)_2} + (n-2)Ph_3P \qquad (1)$$

Recently, Ishii et al.[2] have reported that α,ω-diols can be converted into lactones with tris(hexadecylpyridinium) 12-tungstophosphate by using H_2O_2 as the oxidant.

On the other hand, the lactonization of diols proceeds along with molecular hydrogen evolution when such ruthenium catalysts as $RuH_2(PPh_3)_4$[3] and $Ru_3(CO)_{12}$[4] are used as catalysts. These methods have an advantage over previous methods with respect to freedom from the need for a stoichiometric amount of oxidants. However, these catalysts are unstable under air, and so the reactions should be carried out under inactive gases.

Heterogeneous catalysts used for the lactonization of α,ω-diols have been reported; such catalysts as Cu,[5] however, require extremely high reaction temperatures, and this selectivity is unsatisfactory.

Pd^0 supported on activated carbon has catalytic activities for the oxidative esterification of such primary alcohols as ethanol under oxygen as an oxidant in the liquid phase.[6] Therefore, palladium (Pd^0) supported catalysts can have a catalytic activity for the oxidative lactonization of α,ω-diols with oxygen. When the oxidative lactonization of butane-1,4-diol with the use of Pd^0 supported on various supports was carried out in the liquid phase, Pd^0 supported on K-L zeolite suspended in N,N-dimethylpropionamide had the highest catalytic activity.[7]



$$\underset{\mathbf{2}}{\underset{OH\qquad\quad OH}{CH_2CH_2CH_2CH_2}} + O_2 \xrightarrow{\text{Pd Zeolite}} \mathbf{3} + 2H_2O \qquad (2)$$

In this work, the influence of the zeolite support on the selectivity to γ-butylolactone and that of reaction variables on the oxidative lactonization of butane-1,4-diol over Pd^0 supported on K-L zeolite were examined. Here, we will describe a facile lactionization of butane-1,4-diol with oxygen as an oxidant, the catalyst being Pd^0 supported on K-L-type zeolite suspended in N,N-dimethylpropionamide ($CH_3CH_2CON(CH_3)_2$).

Experimental

Catalyst Preparation. Palladium-exchanged zeolites were prepared from Na^+-exchanged zeolites (Na-A, Na-ZSM-5, Na-X, and Na-Y), Ca^{2+}-exchanged A-type zeolite (Ca-A), and K^+-exchanged L-type zeolite (K-L) using a conventional ion-exchange procedure with an aqueous solution of $[Pd(NH_3)_4]Cl_2$ at room temperature. These zeolites were obtained from the Toso Manufacturing Co. K^+-exchanged X and Y zeolites were prepared from Na-X and Na-Y using a conventional ion-exchange procedure with an aqueous solution of KCl at 343 K. Pd^0 supported on zeolites was prepared as follows: the zeolites exchanged with $[Pd(NH_3)_4]^{2+}$ were heated under air at 623 K for 1 h and then treated with hydrogen at various temperatures. The palladium loading of each catalyst and the degree of K^+-exchange were determined by means of atomic absorption spectrophotometry.

Apparatus and Procedure. Butane-1,4-diol, pentane-1,5-diol, and such solvents as N,N-dimethylpropionamide were obtained from commercial sources and were used without further purification.

The oxidative lactonization was performed in a 50 ml three-necked flask equipped with a condenser and a magnetic stirrer. The catalyst (0.50 g) in 3.00 ml of a solvent and 22.5 mmol (2.00 ml) of butane-1,4-diol or 19.8 mmol (2.00 ml) of pentane-1,5-diol was stirred under oxygen at 357—391 K for 24 h. The conversion of butane-1,4-diol **2** (or that of pentane-1,5-diol **4**) and yield of γ-butyrolactone **3** (or that of δ-valerolactone **5**) were determined with a gas chromatograph (2.0 m Prapak Q column) by using 3-methylbutan-1-ol as the internal standard.

The adsorption of butane-1,4-diol on Pd^0 supportrd on zeolites was carried out in N,N-dimethylpropionamide or H_2O at 301 K for 24 h. The weight of the zeolite on which Pd^0 was supported was 0.500 g, while the butane-1,4-diol and N,N-dimethylpropionamide amounted 49.5 mmol (5.00 ml) and 5.00 ml respectively. The amount of adsorbed butan-1,4-diol was obtained by subtracting the concentration of the butane-1,4-diol determined with a gas chromatograph after the adsorption from the initial concentration of butane-1,4-diol.

Results and Discussion

Activities of Supported Palladium Catalysts. The catalytic activities of Pd^0 supported on zeolites were compared when the oxidative lactonization of butane-1,4-diol **2** was carried out in N,N-dimethylpropion-

Table 1. The Catalytic Activities of Pd^0 Supported on Zeolites

Support	Si/Al	Maximum pore size/nm	Pd/wt%	Solvent	Conversion of **2**/%	Yield of **3**/%	Selectivity to **3**/%
Na-A	1.0	0.42	0.6	NMP	19.2	6.7	36.1
Ca-A	1.0	0.49	0.1	NMP	53.7	16.9	31.5
Na-ZSM-5	52	0.54	5.9	NMP	86.2	81.0	94.0
K-L	3.2	0.71	5.5	No solvent[a]	21.3	2.1	9.8
				NPA	99.4	91.1	91.5
				NPA[b]	1.3	0	0
				NMP	81.4	80.1	98.4
				H_2O[c]	51.3	23.4	45.6
				NPA[c]	88.3	72.5	82.1
Na-X	1.4	0.74	5.6	NMP	79.9	52.0	65.1
K-X[d]	1.4	0.74	5.3	NMP	74.5	63.0	84.6
Na-Y	2.8	0.74	6.0	No solvent[a]	88.4	5.7	6.4
				NPA	95.4	63.6	66.7
				NMP	80.1	52.2	65.2
K-Y[e]	2.8	0.74	5.1	NPA	94.6	79.4	83.9
				NMP	82.8	67.3	81.3

Reaction was carried out under oxygen (101 kPa) at 391 K for 24 h. Catalyst weight: 0.500 g; butane-1,4-diol: 22.5 mmol (2.00 ml); solvent: 3.0 ml. NPA=*N,N*-dimethylpropionamide, NPA=*N*-methylpyrrolidin-2-one. a) Butane-1,4-diol 56.2 mmol (5.00 ml). The solvent was not used. b) Reaction was carried out under nitrogen (101 kPa). c) Reaction temperature was 373 K. d) K^+ (93% exchanged)-X zeolite. e) K^+ (91% exchanged)-Y zeolite.

Table 2. The Amount of Butane-1,4-diol Adsorbed on Pd^0 Supported on Zeolites

Support	Pd^0/wt%	Solvent	Amount of butane-1,4-diol adsorbed/mmol g^{-1}
K-L	5.5	NPA	4.0
		H_2O	1.1
Na-X	5.6	NPA	1.9
K-X[d]	5.3	NPA	2.8
Na-Y	6.0	NPA	2.1
K-Y[e]	5.1	NPA	2.9

The adsorption of butane-1,4-diol was carried out at 301 K for 24 h. The weight of zeolite on which Pd^0 was supported was 0.500 g. Butane-1,4-diol: 49.5 mmol (5.00 ml); NPA (*N,N*-dimethylpropionamide) or H_2O: 5.00 ml. d) and e) See Table 1.

amide or *N*-methylpyrrolidin-2-one under oxygen at 391 K. The catalysts were calcined under air at 623 K for 1 h and were then treated with hydrogen at 623 K for 1 h. As is shown in Table 1, Pd^0 supported on K-L-type zeolite (Pd^0–K-L) has the highest yield of **3** in *N,N*-dimethylpropionamide. That is, the yield of **3** was 91.1% (the selectivity to **3** was 91.5%) when the conversion of **2** was 99.4%.

ZSM-5, K-L, Na-X, and Na-Y type zeolites whose pore sizes are 0.54—0.74 nm have higher catalytic activities than those Na-A and Ca-A type zeolites whose pore sizes are narrow (0.4—0.5 nm). K-L zeolite has nearly the same pore size as Na-X and Na-Y. In order to show the influence of the K^+ in zeolite on the catalytic activity, the reaction was carried out over Pd^0 supported on K^+ (91% exchanged)-Y and K^+ (93% exchanged)-X zeolites. The yield of **3** and the selectivity to **3** increased by exchanging Na^+ with K^+ in a zeolite.

In every case, **3** could not be produced at all under nitrogen. This result shows that oxygen is essential in this reaction system. The Pd^{2+}-exchanged K-L-type zeolite, which was not treated with hydrogen, showed very little catalytic activity, even under oxygen. It is clear that the reduction of Pd^{2+} to Pd^0 with hydrogen is indispensable for the appearance of the catalytic activity.

When the reaction was carried out over Pd^0 (5.5 wt%)–K-L without any solvent and under oxygen, the conversion of **2** and the yield of **3** were 21.3% and 2.1% respectively. The catalytic activity of Pd^0–K-L in H_2O as a solvent at 373 K was lower than that in an organic solvent, *N,N*-dimethylpropionamide, as is shown in Table 1. We have previously reported that the selection of solvent is essential.[7]

The high catalytic activity of Pd^0 supported on K-L zeolite might be attributed to the adsorption property of butane-1,4-diol on zeolite in a solvent. The amount of butane-1,4-diol adsorbed on zeolites was examined under nitrogen in *N,N*-dimethylpropionamide or H_2O for 24 h. The adsorption temperature was 301 K. Under these adsorption conditions, hardly any γ-butyrolactone was detected. As is shown in Table 2, the amount of butane-1,4-diol on Pd^0–K-L in *N,N*-dimethylpropionamide adsorbed was more than that on Pd^0 supported on Na-X, Na-Y, K-X, and K-Y, being 4.0 mmol g^{-1}. It decreased to 1.1 mmol g^{-1} in H_2O. The amount of butane-1,4-diol adsorbed increased when Na^+ was exchanged with K^+ in X and Y zeolites. The order of catalytic activity for the oxidative

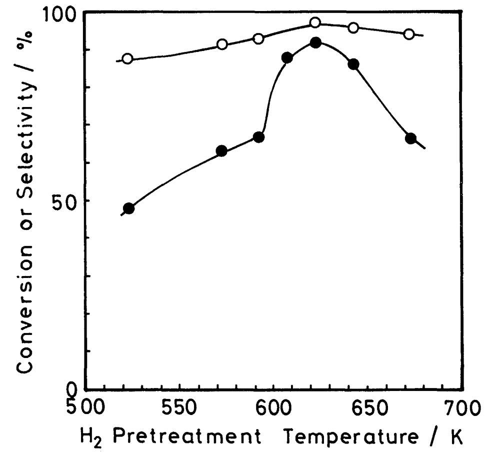


Fig. 1. Effect of the reduction temperature with hydrogen on the conversion of butane-1,4-diol (●) and the selectivity to γ-butyrolactone (○) over Pd^0 (5.0 wt%)-K-L for oxidative lactonization of butane-1,4-diol with oxygen in *N,N*-dimethylpropionamide. Reaction was carried out under oxygen at 391 K for 24 h. Catalyst was calcined under air at 623 K for 1 h before hydrogen treatment at each temperature for 1 h. Catalyst weight is 0.50 g. Butane-1,4-diol is 22.5 mmol. Solvent is 3.0 ml.

lactonization over Pd^0 supported on L-, X-, and Y-type zeolites is the same as that of the amount of butane-1,4-diol adsorbed on them. The explanation for the highest catalytic activity over Pd^0–K-L, is that the amount of butane-1,4-diol can be adsorbed on Pd^0–K-L more than on Pd^0 supported on other zeolites.

The Pd^0–K-L catalyst is also effective for the oxidative lactonization of pentane-1,5-diol **4** into δ-valerolactone **5**. Thus, 0.5 g Pd^0 (5.5 wt%)-K-L gave a 54.6% yield and a 90.8% selectivity in *N,N*-dimethylpropionamide at 391 K for 24 h.

Effect of Reduction Temperature. The effect of the reduction temperature with hydrogen on the catalytic activities of Pd^0 (5.0 wt%)-K-L for the oxidative lactonization of **2** was examined at 391 K for 24 h. The catalyst was calcined under air at 623 K for 1 h before treatment with hydrogen. As is shown in Fig. 1, the conversion of **2** increased as the hydrogen-reduction temperature increased, reaching a maximum at 623 K, where the conversion of **2** was 92.8%. The conversion gradually decreased as the reduction temperature increased. The selectivity to **3** was only slightly influenced by the hydrogen-reduction temperature, being more than ca. 90% at each reduction temperature. For example, it was 96.7% at 623 K, the reduction temperature which gave the highest yield of **3**.

Influence of Reaction Temperature. Figure 2 shows the influence of the reaction temperature on the conversion of **2**, the yield of **3**, and the selectivity to **3**. The conversion of **2** gradually increased as the reaction temperature increased, reaching 98.7% at 391 K. The selectivity to **3** (the yield of **3**) increased sharply above 373 K. The selectivity was ca. 65% below 373 K and ca. 90% above 373 K.

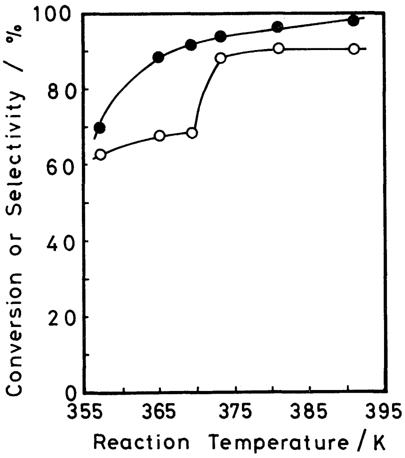


Fig. 2. Influence of the reaction temperature on the conversion of butane-1,4-diol (●), and the selectivity to γ-butyrolactone (○) over Pd^0 (6.6 wt%)-K-L zeolite. Catalyst was calcined under air at 623 K for 1 h and was then treated with hydrogen at 623 K for 1 h. The other reaction conditions: See Fig. 1.

In this oxidative lactonization, H_2O is formed (Eq. 2). Pd^0–K-L suspended in H_2O has a lower catalytic activity than that in *N,N*-dimethylpropionamide at 373 K, as is shown in Table 1. As has been described above, the amount of **2** adsorbed on Pd^0–K-L in H_2O was smaller than that in *N,N*-dimethylpropionamide (Table 2). The explanation for the low catalytic activity for the formation of **3** at temperatures lower than 373 K is that the H_2O formed retards the adsorption of **2** on the catalyst. The oxidative lactonization of **2** over Pd^0 supported on zeolites had better be carried out at more than the boiling point of H_2O in order to remove the formed H_2O from the reaction system.

Advantages of Pd^0 Supported on K-L Zeolite. The advantages of Pd^0 supported on zeolites may be summarized as follows: (1) Pd^0–K-L has a high catalytic activity and a high selectivity for the lactonization of butane-1,4-diol. (2) Molecular oxygen can be used as a convenient oxidant. (3) The catalyst can be easily separated from the product. (4) Third compounds such as PPh_3 are not necessary. (5) The catalyst can be handled in an ambient atmosphere.

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