

Liquid-phase Lactonization of Butane-1,4-diol into γ -Butyrolactone over Palladium supported on K-L Zeolite

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Pd⁰ supported on K-L zeolite suspended in the liquid phase has a high catalytic activity and a high selectivity for the oxidative esterification of butane-1,4-diol into γ -butyrolactone under oxygen at 391 K.

The reported methods for oxidative condensation of 1,4- and 1,5-diols to give the corresponding lactones are mainly limited to homogeneous catalysts such as Pd(OAc)₂¹ or tris(cetylpyridinium)-12-tungstophosphate.² These catalysts require stoichiometric amounts of oxidants such as bromobenzene and more than stoichiometric amounts of oxidants such as H₂O₂. RuH₂(PPh₃)₃³ also has a catalytic activity for the oxidative transformation of 1,4- and 1,5-diols to the corresponding lactones by dehydrogenation in the presence of a hydrogen acceptor such as acetone. On the other hand, heterogeneous catalysts used for the transformation of alcohols into lactones have been reported; catalysts such as Cu⁴ or CuO,⁵ however, require extremely high reaction temperatures and their selectivity is unsatisfactory. Both in the vapour phase and in the liquid phase, Pd⁰ supported on activated carbon⁶ has catalytic activities which result in the oxidative esterification of primary alcohols, such as ethanol, under oxygen as an oxidant.

For the first time we have found that Pd⁰ supported on zeolites has a high catalytic activity and a high selectivity for lactonization of butane-1,4-diol into γ -butyrolactone in the liquid phase, under oxygen, at 391 K.

Palladium ion-exchanged zeolites were prepared from Na⁺-exchanged zeolites (Na-A, Na-ZSM-5, Na-X, Na-Y), Ca²⁺-exchanged A type zeolite (Ca-A), and K⁺-exchanged L type zeolite (K-L), using a conventional ion-exchange procedure with a [Pd(NH₃)₄]Cl₂ solution, at room temperature. These zeolites were obtained from Toyo Soda Manufacturing

Co. Pd⁰ supported on zeolites was prepared as follows: the zeolite exchanged with [Pd(NH₃)₄]²⁺ was heated in air at 623 K for 1 h and then was treated with hydrogen at 623 K for 1 h. Palladium supported on activated carbon and on silica were prepared as follows: activated carbon was impregnated with [Pd(NH₃)₄]Cl₂ solution and silica was exchanged with [Pd(NH₃)₄]²⁺ in NH₃ solution. The activated carbon and silica were pretreated in the same way as the zeolite. The degree of exchange of palladium was determined by atomic absorption analysis. The lactonization was performed for 24 h, in a 50 ml three-neck flask equipped with a condenser and a magnetic stirrer. The catalyst (0.500 g) in 3.00 ml of solvent, such as *N,N*-dimethylpropionamide, and 22.5 mmol (2.00 ml) of butane-1,4-diol were stirred under oxygen at 391 K for 24 h. The conversion of butane-1,4-diol and yield of γ -butyrolactone were determined with a gas chromatograph (2.0 m Prapak Q column), using 3-methylbutan-1-ol as a standard.

Table 1 shows the catalytic activities of Pd⁰ supported on zeolites in various solvents, such as *N*-methylpyrrolidin-2-one. Pd⁰ supported on K-L zeolite (Pd-K-L) gives the highest yield of γ -butyrolactone (91.1%) in *N,N*-dimethylpropionamide; the conversion of butane-1,4-diol was 99.4% and the selectivity to γ -butyrolactone was 91.5%. When the reaction was carried out without a solvent, the conversion of butane-1,4-diol and yield of γ -butyrolactone were 21.3% and 2.1%, respectively. In every case, γ -butyrolactone could not be produced under nitrogen. Pd²⁺-exchanged K-L zeolite, which was not reduced with hydrogen, has very little catalytic activity

Table 1. The catalytic activities of Pd⁰ supported on zeolites.^a

Support	Si/Al	Maximum pore size/ nm	Pd/ wt%	Solvent ^b	Conversion of butane-1,4-diol/ %	Yield of γ - butyrolactone/ %	Selectivity/ %
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	DMP	85.5	52.1	61.7
				NMP	86.2	81.0	94.0
K-L	3.2	0.71	5.5	None ^c	21.3	2.1	9.8
				DMP	99.4	91.1	91.5
				NMP	81.4	80.1	98.4
				NMP	79.9	52.0	65.1
Na-X	1.4	0.74	5.6	None ^c	88.4	5.7	6.4
Na-Y	2.8	0.74	6.0	DMF	66.0	38.1	57.7
				DMA	71.8	46.3	64.5
				DMP	95.4	63.6	66.7
				NMP	80.1	52.2	65.2
				DMG	96.4	38.4	39.8
				DEG	98.7	34.5	43.9
				DMP	47.1	18.2	38.6
				DMP	72.3	31.4	43.4
Activated carbon			4.3	DMP	47.1	18.2	38.6
SiO ₂			5.1	DMP	72.3	31.4	43.4

^a Reaction conditions: catalyst 0.50 g; reaction temperature 391 K; reaction time 24 h; butane-1,4-diol 22.5 mmol (2.00 ml); solvent 3.00 ml.

^b NMP = *N*-methylpyrrolidin-2-one; DMP = *N,N*-dimethylpropionamide; DMF = *N,N*-dimethylformamide; DMA = *N,N*-dimethylacetamide; DMG = diethylene glycol dimethyl ether; DEG = diethylene glycol diethyl ether. ^c Butane-1,4-diol 56.2 mmol (5.00 ml). No solvent was used.

under oxygen. Thus, the conversion of butane-1,4-diol was 13.8% and the yield of γ -butyrolactone was 2.4%, in *N,N*-dimethylpropionamide. Zeolites ZSM-5, K-L, Na-X, and Na-Y, whose pore sizes are 0.54–0.74 nm, have higher catalytic activities than those (Na-A and Ca-A) whose pore sizes are narrower (0.4–0.5 nm). Pd⁰ supported on activated carbon (Pd-C) and silica, as shown in Table 1, gave lower catalytic activities than zeolites such as Pd-K-L. Thus, Pd-C gave 47.1% butane-1,4-diol conversion and an 18.2% yield of γ -butyrolactone (38.6% selectivity).

It was also possible to apply Pd-K-L to the lactonization of pentane-1,5-diol into δ -valerolactone. Thus, 0.50 g of Pd (5.5 wt%)-K-L gave a 54.6% yield and 90.8% selectivity in *N,N*-dimethylpropionamide at 391 K for 24 h.

When Pd(OAc)₂ was used as a homogeneous catalyst for the oxidation of butane-1,4-diol to γ -butyrolactone, a stoichiometric amount of bromobenzene was required as oxidant and potassium carbonate was employed as a base.¹ Moreover, PPh₃ was found to be necessary. It has been reported also that RuH₂(PPh₃)₄ showed catalytic activities for the oxidative transformation of diols to lactones.³ In this method, hydrogen acceptors such as acetone should be used owing to the evolution of molecular hydrogen.

The features of Pd⁰ supported on zeolites may be summarized as follows: (i) Pd-K-L has a high catalytic activity and a high selectivity for the lactonization of butane-1,4-diol into γ -butyrolactone; (ii) molecular oxygen can be used as a convenient oxidant; (iii) the catalyst can be easily separated from the product; (iv) a third compound, such as PPh₃, should not be added to the reaction system.

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References

- 1 Y. Tamaru, Y. Yamada, K. Inoue, Y. Yamamoto, and Z. Yoshida, *J. Org. Chem.*, 1983, **48**, 1286.
- 2 Y. Ishi, T. Yoshida, K. Yamawaki, and M. Ogawa, *J. Org. Chem.*, 1988, **53**, 5549.
- 3 S. Murahashi, T. Naota, K. Ito, Y. Maeda, and H. Taki, *J. Org. Chem.*, 1987, **52**, 4319.
- 4 K. Takeshita, S. Nakamura, and K. Kawamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2622.
- 5 B. Berthon, A. Forestiere, G. Leleu, and B. Sillion, *Tetrahedron Lett.*, 1981, **22**, 4073.
- 6 T. Kunugi, T. Kono, and Y. Shinohara, *Nippon Kagaku Zasshi*, 1973, 454; T. Kunugi, T. Kono, M. Yanagusawa, and H. Arai, *ibid.*, 1972, 223.