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Formation of an intermetallic compound Pd_3Te with deactivation of Te/Pd/C catalysts for selective oxidation of sodium lactate to pyruvate in aqueous phase

H. Hayashi [1], S. Sugiyama, N. Shigemoto, K. Miyaura [a], S. Tsujino,
K. Kawashiro and S. Uemura [b]

Department of Chemical Science and Technology, University of Tokushima,
Minamijosanjima, Tokushima 770, Japan
[a] *Shikoku Research Institute Inc., Yashima-nishi, Takamatsu 761-01, Japan*
[b] *Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University,*
Yoshida, Kyoto 606, Japan

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The addition of a trace amount of Te promoted the activity of Pd/C in the liquid-phase oxidation of lactic acid, but the Te/Pd/C catalyst, for which Pd_3Te crystalline phase extended over the bulk at a higher Te-doping above Te/Pd = 0.3 (atom), was again inactive. A powder XRD evidence for Pd_3Te is given.

Keywords: XRD; Pd_3Te; deactivation; liquid-phase oxidation; sodium lactate

1. Introduction

A variety of catalyst modifications for palladium and platinum have been proposed in both oxidation and reduction. Smits et al. [1] demonstrated by the oxidation of D-gluconic acid that the primary hydroxyl group was preferentially oxidized on Pt/C, while the preference dramatically changed on Pb/Pd/C toward oxidation at the position α to the carboxyl group. Lindlar catalysts, $Pb/Pd/CaCO_3$ [2,3] and $Pb/Pd/SiO_2$ [4], hydrogenate acetylenes selectively to olefins. The catalyst Te/Pd/C was established in a commercial scale [5] for oxidation of butadiene to tetrahydrofuran through 1,4-diacetoxy-2-butene [6]. In the previous work, we observed no absorption of oxygen in the attempted oxidation of lactic acid on Pd/C, while a spectacular change in oxidation activity in favor of pyruvic acid was observed in the presence of Pb/Pd/C, Te/Pd/C and related catalysts [7]. The cata-

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[1] To whom correspondence should be addressed.

lysts Pb/Pd/C and Bi/Pd/C were also used for oxidation of 1-methoxy-2-propanol to 1-methoxy-2-propanone [8].

Additives employed above such as lead, bismuth, antimony, tellurium and selenium are post-transition metals or semi-metals having more or less covalent nature, and often show unusual effects on metallic catalysts.

Formation of an alloy or intermetallic compound Pd_3Pb covering the surface layer of palladium crystallites has been claimed for Lindlar catalysts, Pb/Pd/$CaCO_3$ [2] and Pb/Pd/SiO_2 [4]. However, much emphasis on the crystalline Pd_3Pb as active species appears to have room for further discussions. Powder X-ray patterns of Pd_3Pb were presented in mineralogy by Cabri and Traill [9], but no distinct reflection indicating Pd_3Pb was observed on Pb/Pd/$CaCO_3$ [2,3] and Pb/Pd/C [7].

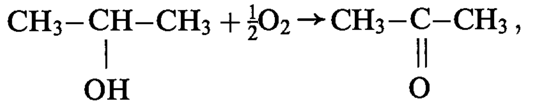
In the present work, an evidence for the formation of Pd_3Te at higher Te-contents in Te/Pd/C is given by the powder XRD patterns, closely corresponding to that reported for Pd_3Te phase by Grønvold and Røst [10]. The addition of a trace amount of Te promoted the activity of Pd/C in the liquid-phase oxidation of lactic acid, but the formation of Pd_3Te resulted in the deactivation of the catalyst.

2. Experimental

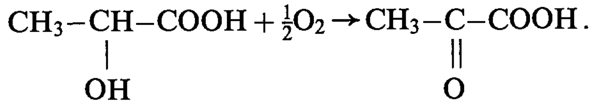
The catalyst Te/Pd/C was prepared by impregnating a commercially available 5% Pd/C (Wako Pure Chemicals, Osaka) with a given amount of TeO_2 dissolved in 6N HCl. The suspension was heated to dryness over a steam bath, and the residue was reduced overnight with formalin and 30% KOH, and finally washed with hot water until the filtrate became neutral. The detailed protocol for catalyst preparation and the reaction procedure for oxidation of lactic acid were described in a previous paper [7]. A binary metal black or Pd–Te system was prepared as described previously [11]. Powder X-ray diffraction of Te/Pd/C and related catalysts was measured by a MXP system of MAC Science Co., Tokyo.

3. Results and discussion

Oxidation of 2-propanol as a model for secondary alcohols (eq. (1)) occurred with great ease on Pd/C to give acetone, but no reaction was observed for lactic acid on the same catalyst [7]:



$$CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3+\tfrac{1}{2}O_2\rightarrow CH_3-\underset{\substack{\|\\ O}}{C}-CH_3\,, \qquad (1)$$



$$CH_3-\underset{\substack{|\\ OH}}{CH}-COOH+\tfrac{1}{2}O_2\rightarrow CH_3-\underset{\substack{\|\\ O}}{C}-COOH\,. \qquad (2)$$

Additives such as Pb, Bi and Te were bound on metallic Pd by a strong interaction. The resultant Pb/Pd/C and Te/Pd/C showed the activity for selective oxidation of lactic acid to pyruvic acid (eq. (2)) as shown in fig. 1a and figs. 1b–1d, respectively. A trace amount of Te as low as an atomic ratio of Te/Pd = 0.02 was enough to afford pyruvic acid (fig. 1b). The promoting effect of Te was similar to that of Pb, but minor, and showed a plateau at Te/Pd = 0.02–0.15 (figs. 1b, 1c). The catalyst Te/Pd/C was inactive at a Te-content above Te/Pd = 0.3 (fig. 1d), while the reference Pb/Pd/C with a high Pb-content of Pb/Pd = 0.6 was still active (fig. 1a).

Powder XRD patterns of Te/Pd/C with various Te-contents, and of Pd/C for reference are compared in fig. 2. These catalysts were used once for the oxidation of lactic acid, filtered, washed with hot water, and then dried in vacuo at room temperature prior to the XRD measurement. Every peak detected for Pd/C (fig. 2a) was assigned to metallic Pd (JCPDS 5-681). With increasing of Te-content up to Te/Pd = 0.15 (figs. 2b and 2c), the pattern appears essentially the same as that of Pd except for the line-broadening. A striking difference in XRD pattern was observed for catalysts of Te/Pd = 0.3 and 1.0 (figs. 2d and 2e). A single peak at the position of Pd(111) ($2\theta = 40.04°$) split into twin peaks, and the others detected at $2\theta = 68°$ and 82° in figs. 2a–2c assignable to Pd disappeared in figs. 2d and 2e, suggesting the formation of a new crystalline phase of the Pd–Te system for Te/Pd/C catalysts with a

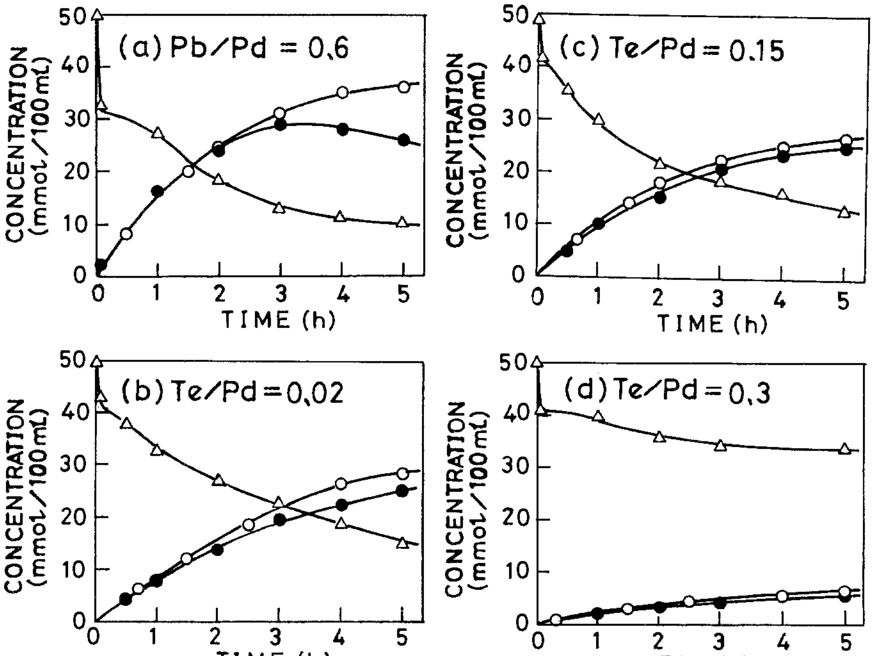


Fig. 1. Oxidation of lactic acid on Pb/Pd/C (a) and Te/Pd/C (b)–(d). Temperature 90°C; catalyst 6 g; pH 8, (△) lactic acid, (●) pyruvic acid, (○) oxygen absorbed ×2.

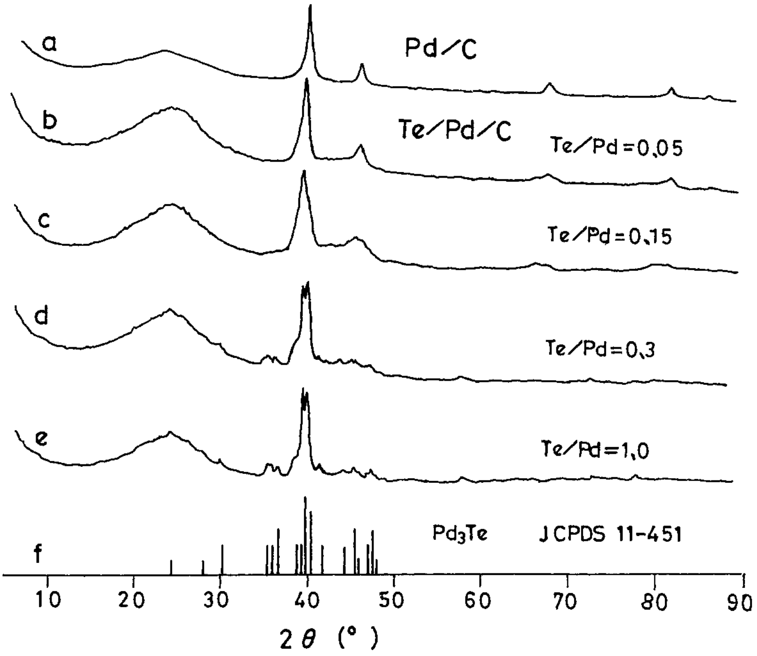


Fig. 2. Powder X-ray diffraction patterns of Te/Pd/C and Pd/C.

higher Te-content. The phase was identified as Pd_3Te(JCPDS 11-451), and the schematic XRD pattern at low angle reflections [10] is given in fig. 2f for reference.

The composition Pd_3Te appears to be a face-centered cubic lattice: 1/2 atom Pd at 6 face-centers (3Pd) with 1/8 atom Te at 8 corners (1Te) per unit cell, but the structure is not yet established. Grøvold and Røst [10] studied extensively the Pd–Te system by X-ray single crystal photographs for alloys with various compositions, where the samples were heated for some days at 600°C, annealed at 250–650°C and cooled slowly to room temperature. Thus, the intermediate phases of Pd_4Te, Pd_3Te, $Pd_{2.5}Te$, Pd_2Te, PdTe and $PdTe_2$ were identified. As usual the initial composition of two metals were adjusted as closely as desired in the preparation of a binary alloy [10]. Arbitrary ingredients give a composite Te–Pd phase as shown in fig. 3. A binary metal black of Te–Pd with a composition of Te/Pd = 0.759 was prepared by the decomposition of a diphenyl telluride–palladium chloride complex in methanol under carbon monoxide atmosphere [11]. The amorphous Te–Pd black (fig. 3a) crystallizes on heating under nitrogen (figs. 3b and 3c), but the resultant crystalline phases were evidently a mixture of some species which were difficult to identify. Among various possibilities for palladium telluride composition, it is of interest to note that only a single phase of Pd_3Te was formed irrespective of the Te-doping in the region above Te/Pd = 0.3 for Te/Pd/C catalysts.

An intermetallic compound of the composition of Pd_3Pb similar to Pd_3Te has been suggested on Pb-modified $Pd/CaCO_3$ [2] and Pd/SiO_2 [4]. However, the only

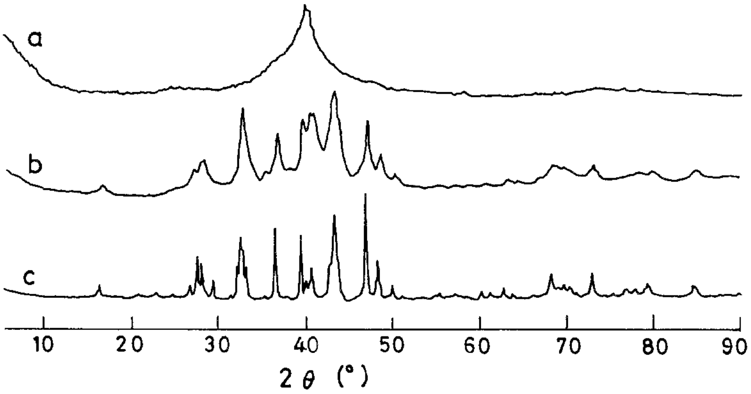


Fig. 3. Powder X-ray diffraction patterns of a binary metal black of Te–Pd (a) and the crystallized samples by heating under nitrogen for 1 h at 200°C (b) and at 300°C (c).

evidence was a slight shift toward lower 2θ of major reflections assigned to Pd, leading to an increase in the lattice parameter closely to the values of 4.013 Å [12] or 4.021_6 Å [13] reported for Pd_3Pb, due to the dissolution of lead in palladium. Thus Pb-modified Pd catalysts are composed of a layer of either a Pb–Pd alloy or intermetallic compound below which there remains the essentially unchanged Pd phase [2,4], and the surface layer is too thin to be visible in X-ray diffraction [4].

Powder XRD does not give direct information about the working catalyst surface, but characterizes the bulk crystalline phase. It is noteworthy that such a Re/Pd/C catalyst, for which the Pd_3Te phase extended over the bulk and was detected by XRD, was inactive for the present oxidation reaction of sodium lactate to pyruvate. The effect of Pb seems to be milder than that of Te, and an excess doping of Pb on Pd/C does not cause the deactivation of Pb/Pd/C (cf. figs. 1a and 1d).

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