Liquid-Phase Oxidation of Propylene Glycol Using Heavy-Metal-Free Pd/C under Pressurized Oxygen

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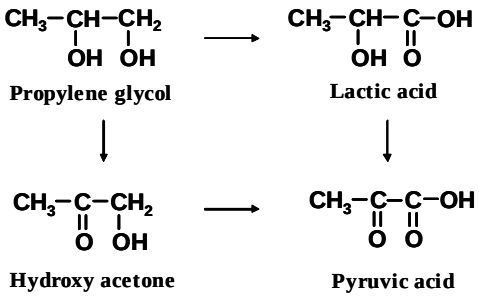
Introduction

In the liquid-phase oxidation of propylene glycol using Pd/C and related catalysts (Scheme 1), it is generally accepted that Pd/C shows the great activity for the production of pyruvic acid through hydroxyl acetone while Pd/C doped with heavy metals or noble metals shows the activities for the formation through lactic acid under atmospheric pressure [1,2]. However it has been recently reported that Pd/C shows the great activity for the conversion of sodium lactate to sodium pyruvate under pressurized oxygen [3,4], indicating that the doping of Pd/C with heavy metals may not be needed in the system. In order to confirm the advantageous effect of the employment of the pressurized oxygen using heavy-metal-free Pd/C, the liquid-phase oxidation of propylene glycol has been examined using Pd/C under pressurized oxygen.



Scheme 1 Oxidation of propylene glycol

Experimental

Into a stainless steel autoclave (85 ml), 25 ml of an aqueous reaction solution containing propylene glycol (12.5 mmol) and solution of NaOH (0 ~ 25 mmol) was added. After the autoclave was filled with 100% O_2, the reaction temperature was adjusted to 358 K in the presence of 5 wt.% Pd/C (0.125g) and the solution was stirred at 700 rpm. In the present study, the pressure in the autoclave was kept to be constant by the addition of 100% O_2 to the autoclave during the reaction. After the reaction was allowed to proceed for 5h, the solution was filtered. The reaction solution thus obtained was analysed with FID-GC.

Results/Discussion

Based on the previous reports [1,2], the oxidation of propylene glycol to pyruvic acid through lactic acid or hydroxyl acetone was strongly dependent on the dopant added to Pd/C. Figure 1 shows the effect of NaOH on the oxidation of propylene glycol under pressurized oxygen (1 kPa) using Pd/C. When an amount of NaOH added into the reaction solution increased, formation of lactic acid tended to increase while that of hydroxy acetone tended to decrease. This also showed that no hydroxy acetone was obtained when the molar ratio of NaOH for propylene glycol was more than 1.0. It should be noted that the conversion of propylene glycol to lactic acid certainly proceeds in the presence of Pd/C under pressurized oxygen conditions, in contrast to the reports reported for the same reaction using Pd/C doped with Pb or Te [1].

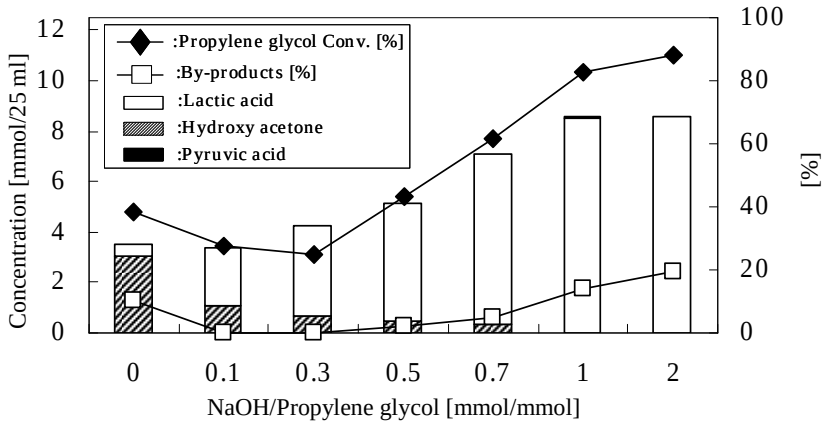


Figure 1. Effect of NaOH on the oxidation of propylene glycol at 1 MPa.

As shown in Fig. 1, pyruvic acid could not be obtained under the present conditions. Since the oxidation of sodium lactate to sodium pyruvate proceeds favourably under the present conditions [3,4], the unreacted propylene glycol may contribute to a side reaction that disturbs the oxidation of lactic acid to pyruvic acid.

References

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