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The Active Hydrogen Electrochemically or Thermally Generated on $Pd/H_3PO_4/Pd$ Catalysts

Kiyoshi OTSUKA* and Ichiro YAMANAKA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

Hydrogenation of 2-propanol into propane was caused by the hydrogen atoms electrochemically generated on Pd-black of the electrocatalytic cell $Pd/H_3PO_4/Pd$. The reaction was also caused by the hydrogen generated through spillover and reverse spillover between Pd and H_3PO_4. Under closed circuit conditions, the latter hydrogenation over the anode Pd was retarded because of the inhibition of the reverse spillover.

The Electrochemically pumped oxygen through an ion-conducting stabilized zirconia often showed an unique catalytic behavior.[1-3] The same may be true for the electrochemically generated hydrogen through proton-conducting electrolytes. In this communication, we describe an unique catalytic behavior of hydrogen electrochemically or thermally generated over $Pd/H_3PO_4/Pd$ catalysts. The reactions of 2-propanol in the presence and absence of hydrogen were chosen as a test reaction. The catalysts consisted of Pd-black attached on both side of the walls of silica wool wafer (1.5 mm in thickness, 21 mm in diameter) which soaked phosphoric acid (85% H_3PO_4, 0.5 ml). The Pd-black (10 mg) were adhered uniformly on each sides of the wafer. The picture of the reactor used and the detailed method for the preparation of the catalyst were described elsewhere.[4] The catalyst $Pd/H_3PO_4/Pd$ was suspended by Pt wires in flow of 2-propanol vapor carried by helium with or without H_2. Water vapor (0.5 kPa) was carried with 2-propanol to keep the electrolyte always being wet with water. The partial pressure of 2-propanol was 1.1 kPa. The flow rate of gas mixture was 51 ml min^{-1}. Quantitative analysis of the products was carried out by gas chromatography. All the experiments were carried out at 80 °C.

Under open circuit conditions in the absence of H_2 in the reactant, the $Pd/H_3PO_4/Pd$ catalyzed only dehydration of 2-propanol giving propylene and diisopropyl ether (IPE). The formation rates of the two products did not depend on the quantities of the Pd-black (0-40 mg) adhered to the wafer. This observation shows that the dehydrations of 2-propanol are catalyzed by the H_3PO_4.

Figure 1 shows the effect of electric current (due to the transport of H^+) on the rates of formations of the products for the $Pd/H_3PO_4/Pd$. A constant current 10 mA (applied potential 1.60 V) was flowed at the time on stream 5.5 h and the circuit was opened at 15 h. The products newly formed under closed circuit were propane, acetone, CO_2, and hydrogen. The quantities of acetone and

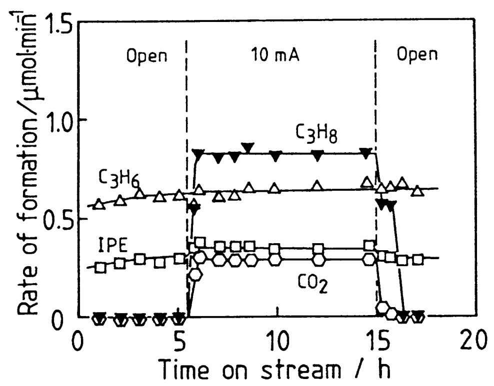

Fig. 1. Effects of current (10 mA) on the reaction of 2-propanol.

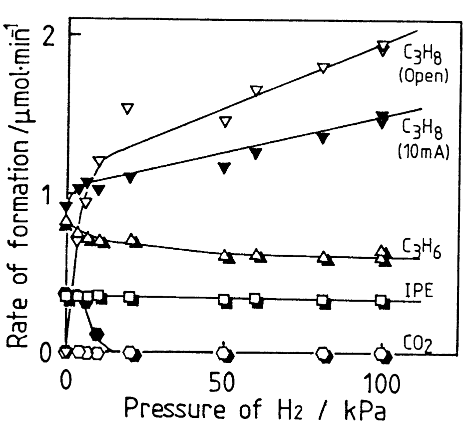

Fig. 2. Effects of $P(H_2)$ on the rates of formations of products under open (unfilled) and closed circuits (filled symbols).

hydrogen were not measured because of difficulties in simultaneous determination of the quantities of all the products. Separate experiments showed that the formation rates of acetone and hydrogen were 1.9 and 2.5 μmol min^{-1} under the same closed circuit conditions as those of Fig. 1. The results in Fig. 1 indicate that the formation rates of C_3H_6 and IPE increase only slightly when the current is flowed. The formation of acetone under the closed circuit conditions can be ascribed to the electrochemical oxidation of 2-propanol on the Pd-black electrode at anode side as follows;

$$\text{Anode;}\quad CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e^- \qquad (1)$$

The formation of CO_2 suggests the further oxidation of acetone at anode side;

$$CH_3COCH_3 + 5H_2O \rightarrow 3CO_2 + 16H^+ + 16e^- \qquad (2)$$

The protons released are transferred across the H_3PO_4 electrolyte to the cathode side by the electric potential applied between the two electrodes. These protons would be discharged on the cathode electrode desorbing as $H_2(g)$.

$$\text{Cathode;}\quad 2H^+ + 2e^- \rightarrow H^* + H^* \rightarrow H_2(g) \qquad (3)$$

The rates of steady-state formations of the acetone and CO_2 under closed circuit conditions were well coincident with the quantities calculated from the current assuming the electrochemical oxidations 1 and 2. However, the quantity of hydrogen evolved was considerably less than those expected from the current. Thus, it is speculated that the nascent hydrogen atoms generated just after the discharge of the H^+ on the Pd-black electrode at the cathode side (denoted as H*) react with 2-propanol giving propane according to the following equation;

$$CH_3CH(OH)CH_3 + 2H^* \rightarrow CH_3CH_2CH_3 + H_2O \qquad (4)$$

This idea explains the formation of propane under the flow of current in Fig. 1.

Under open circuit conditions, it was found that the $Pd/H_3PO_4/Pd$ catalyzed hydrogenation of 2-propanol into propane when hydrogen was present in the gas phase. The reaction did not take place at all when Pd or H_3PO_4 was used alone as the catalyst. The effects of the partial pressure of hydrogen, $P(H_2)$, on the formation rates of C_3H_8, C_3H_6, and IPE using the $Pd/H_3PO_4/Pd$ under open circuit conditions are shown in Fig. 2 with the unfilled symbols. The rate of IPE-formation was not influenced by the addition of hydrogen. The rate of C_3H_6-formation decreased slightly when hydrogen was added. The former observation strongly suggests that the acidity or acid strength of the catalysts is not influenced by hydrogen. Since the catalytic formation of C_3H_6 over H_3PO_4 should not be influenced by hydrogen, the latter observation must be ascribed to the hydrogenation of C_3H_6 to C_3H_8. However, the increase in the rate of C_3H_8-formation(▽) cannot be ascribed to the hydrogenation of C_3H_6 because the rate of C_3H_6-formation decreases only slightly with $P(H_2)$. Thus, it is concluded that the C_3H_8 is mainly formed through direct hydrogenation of 2-propanol.

The effects of $P(H_2)$ on the formation rates of C_3H_8, C_3H_6, and IPE were also measured under constant current of 10 mA. The results are plotted in Fig. 2 with the filled symbols. Neither acetone nor CO_2 was produced in the presence of H_2 greater than 10 kPa. Thus, the current flowed under the $P(H_2)$ greater than 10 kPa can be ascribed wholly to the electrochemical pumping of hydrogen. As can be seen in Fig. 2 the formation rates of $C_3H_6$and IPE were not influenced much by the hydrogen pumping in the presence of gaseous H_2. In the absence of H_2 in the reactant, these rates were not influenced much by the flow of current, either (Fig. 1). These results suggest that the hydrogen pumping does not affect the acid character of the Pd/H_3PO_4/Pd. However, the hydrogen pumping affected the rate of C_3H_8-formation remarkably when hydrogen was not added in the reactants ($P(H_2)=0$ in Fig. 2). The partial pressure of hydrogen calculated from the current (10 mA) and the rate of C_3H_8-formation (0.82 μmol min^{-1}) was 0.12 kPa. Under open circuit conditions, hydrogen pressure of 8 kPa was required to get the same formation rate of C_3H_8 as can be seen in Fig. 2. These observations indicate that the hydrogen atoms effective for hydrogenation of 2-propanol can easily be generated electrochemically through the H_3PO_4 compared to those generated thermally under open circuit conditions.

It seems reasonable to consider that hydrogenation of 2-propanol under open circuit conditions results from hydrogen atoms adsorbed on the surface of Pd-black. However, as described earlier, the reaction did not occur over Pd or H_3PO_4 alone. The combination of Pd with H_3PO_4 was necessary to catalyze the reaction. These facts suggest that the active hydrogen atoms are also generated thermally when Pd is contacted with H_3PO_4. Although the detailed mechanism for the activation of hydrogen is not known at the moment, spillover and reverse spillover of hydrogen atoms5) between the metal and electrolyte may explain the generation of active hydrogen on the Pd-black.

Figure 3 shows the effect of current on the rates of products at $P(H_2)$ of 98 kPa. The rate of C_3H_8-formation decreased with a rise in the current to 10 mA, but the rate increased above this current. The formation rates of C_3H_6 and IPE increased only slightly with a rise in the current. The unexpected decrease in the rate of formation of C_3H_8 can be explained well in terms of the pictures in Fig. 4 as follows. Under open circuit conditions (Fig. 4-(a)), the hydrogenation of 2-propanol was caused by the H* generated through spillover and reverse spillover of hydrogen between the H_3PO_4 and Pd-black on both sides of the wafer. However, under closed circuit conditions (Fig. 4-(b)), the reverse spillover of

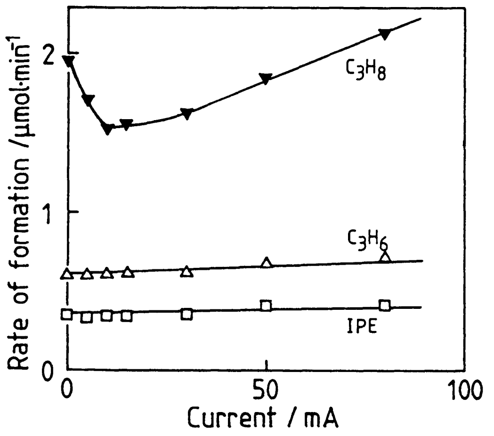

Fig. 3. Effects of current on the rates of formations of the products.

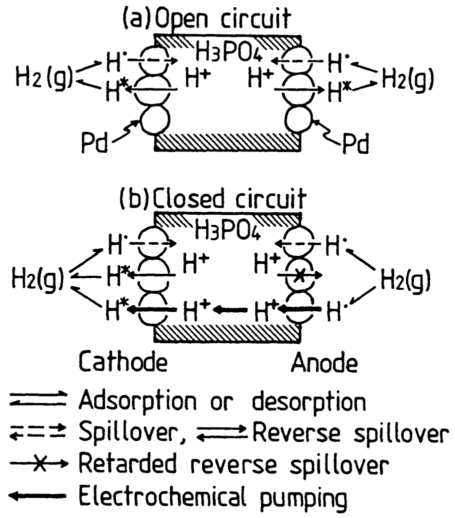

Fig. 4. Models for activation of hydrogen under open and closed circuit conditions.

hydrogen at anode are retarded by the electric overpotential applied between the anode Pd and the electrolyte. This effect must depend on the current or the electric potential. Thus, the decrease in the rate of C_3H_8-formation until 10 mA in Fig. 3 can be ascribed to the retardation of the reaction over the Pd-black of anode side. This idea has been supported by the separate experiments using Pd-black and Au-meshes as electrodes. Preliminary experiments showed that the Au-meshes did not catalyze hydrogenation of 2-propanol in the presence of H_2 of 98 kPa. The Au(cathode)/H_3PO_4/Pd(anode) cell catalyzed the hydrogenation of 2-propanol under open circuit conditions at $P(H_2)$ of 98 kPa. However, under constant current of 10 mA, the reaction was retarded completely. These results suggest that hydrogenation of 2-propanol on the anode Pd-black for the Pd/H_3PO_4/Pd (Fig. 3) must be inhibited at the current of 10 mA. Thus, the increase in the formation rate of C_3H_8 above 10 mA can be ascribed wholly to the reaction due to the H* electrochemically generated on the cathode Pd-black. The observation in Fig. 2 that the rate of C_3H_8-formation under closed circuit conditions (▼) is lower than that for open circuit conditions (▽) at $P(H_2) > 10$ kPa can be explained in terms of the idea that the former reaction occurs only on the cathode Pd but the latter occurs on the Pd on both sides.

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