Catalytic Reactions of *cis*-2-Butene at the Solid-Solid Interface of Ferroelectrics and Metals under an Electric Field

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Catalytic reactions at the solid-solid interface of ferroelectrics and an electrode of metal catalyst under an electric field were studied. For the reactions of *cis*-2-butene under hydrogen, the selectivity and conversion of the formation of *n*-butane and *trans*-2-butene changed under an applied electric field. We showed theoretically that with increasing electric field the aperture size at the interface was reduced, influencing the catalytic reactions. The ability to actively control the aperture size with an electric field promises novel applications of catalytic systems.

Much research on the influence of electrical effects on catalytic reactions has been done,[1-4] of which main subject is electrolytic reactions. For example, the formation of benzene from *p*-benzoquinone over a silver catalyst proceeds under an electric current. The oxidative reaction accompanies a reduction of Ag^+ to inactive Ag^0, which is oxidated to active Ag^+ by an electric current.[4] These electrically-enhanced reactions were mainly developed for transporting electrons or small molecules for recycling redox processes.

We developed a new system that uses electrical fields to control small space, much important factor, over catalytic active site, enhancing catalytic reactions. We developed a solid-solid interface of ferroelectrics and an electrode of metal catalyst with surface roughness (Ra) on the order of nanometers. Under an imposed electric field, the interface contracts due to a strong electrostatic force. This causes a change of the interface-aperture of which wall is the catalytic site. A control of gas permeation through the interface-aperture changed by an electric field has previously been successfully demonstrated.[5, 6] Here, we report the first demonstration of catalysis induced by electrically-controlled aperture change. Reactions of *cis*-2-butene under hydrogen over palladium were studied with our new system.

At a pressure, *P*, of about 1×10^{-3} Pa, Pd was deposited onto the surface of a stainless-steel (SS; Ra= 1.0 nm) plate, which had a small hole in the middle (Figure 1). The shape of the deposited Pd film was a disk with a thickness of 70-80 nm and with a diameter of 16 mm. We used a lead zirconate titanate disc (PZT; thickness: 300 μm; diameter; 20 mm; relative dielectric constant: 550; and surface roughness, Ra= 6.5 nm) for the ferroelectric material. The PZT disc was laid in the middle on the Pd-deposited SS so that it completely covered the Pd thin film. Then, the PZT/Pd/SS catalyst system was put in a glass chamber. An electrode was connected to an Al vapor-exposed upper face of the PZT disc. An electric field can be imposed between the upper face of the PZT disc and the SS plate through an external power supply.

A mixture of *cis*-2-butene and hydrogen gas (1:1) was introduced into the upper part of the chamber in the pressure range of 10 ~ 60 mmHg. The gases diffuse through the interface of the PZT disc and Pd film surfaces. While diffusing, the gas molecules collide with the Pd surface and react with a certain probability. Unreacted gases and products are drawn through the hole in the SS plate to the lower part of the chamber. Under an applied electric voltage, very small asperities at the PZT/Pd film contact interface are deformed by tribology effects, due to the large electrostatic force. This causes the small space at the interface to contract, which increases the catalytic reaction rate of gases.

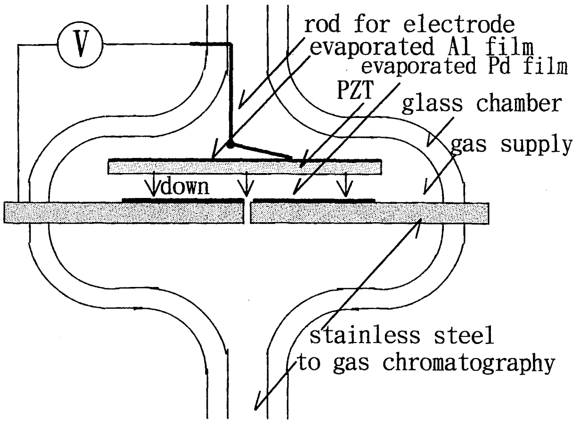

Figure 1. Schematic of catalytic system.

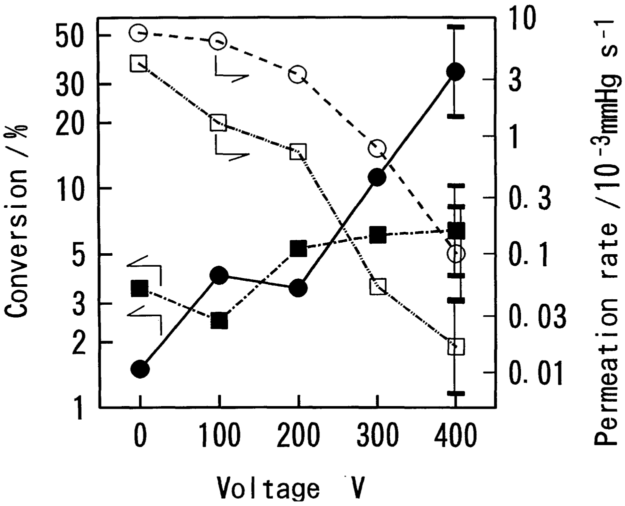

Figure 2. Conversion to *n*-butane (●) and *t*-2-butene (■) and permeation rates of H_2 (○) and *c*-2-butene (□) as a function of applied voltage at 20 mmHg. The outlet pressure : 0-0.2 mmHg.

Permeated gases were analyzed using gas chromatography (GC; column: Unicarbon A-400, GL Sciences Co., Ltd.) after liquid nitrogen-trapping. The permeation rates were also measured with a diaphragm vacuum gauge and the same GC.

Over a Pd catalyst, the formation of *n*-butane by addition of hydrogen to *cis*-2-butene and a formation of *trans*-2-butene by isomerization of *cis*-2-butene proceed at room temperature. Figure 2 shows the permeation rates of *cis*-2-butene and hydrogen in steady state. We observed that with increasing electric voltage in the range of 0 ~ 400 V, both permeation rates decreased, especially in the higher voltage range. Permeation of H_2 was predominantly Knudsen type through inorganic membranes having pores of several nm and in the same pressure range as the present experiments.[7-10] The mean free path of H_2 is larger than that of *cis*-2-butene.[11] From values of the surface roughnesses of Pd thin film and PZT, we estimated our aperture size to be 3 ~ 30 nm. This strongly suggests that the permeation mechanism of hydrogen and *cis*-2-butene in our catalyst is a mixture of Poiseuille and Knudsen transport.

Figure 2 also shows the conversion of *cis*-2-butene to *n*-butane and to *trans*-2-butene in steady state. We observed that the voltage from 0 to 400 V increased the conversion to *n*-butane by a factor of 20, while within experimental error, conversion to *trans*-2-butene did not increase significantly. Therefore, both the conversion and selectivities of the two reactions were found to change under an electric field. The changes in the conversion and the permeation rates were reversible. The weak dependence on voltage of the conversion of *cis*-2-butene to *trans*-2-butene is not due to the equilibrium of *cis*- and *trans*-2-butenes, which yields a conversion of about 50%.[12]

We can explain the change in the conversion and the selectivities from the basis of the field-induced aperture change. First, the increase in conversion with increasing electric voltage is explained next. The frequency of collision of one gas molecule with Pd surface during its travel from the inlet of the interface to the outlet, *F*, increases with the field-induced decrease in the aperture, yielding the increase in conversion. Second, the change in selectivities is explained next. The kinetics and mechanism of hydrogenation and isomerization of *cis*-2-butene under hydrogen over Pd/ α-Al_2O_3 have been examined.[12-14] Both reactions possibly proceed via 2-butyl adsorbate.[14] Near room temperature orders of reaction for formation of *n*-butane are 0.5 and 0 for pressure of hydrogen and *cis*-2-butene, and those for formation of *trans*-2-butene are 0.07 and 0 respectively. A relation of a conversion (low conversion) versus *F* for the conditions of our experiments, is equivalent to that of a reaction rate versus *P* for the conditions of the above previous experiments. Therefore, we obtain:

$$C_{NB} = k_1 \; F_H^{0.5} \; F_{CB}^{0} \tag{1}$$

$$C_{TB} = k_2 \; F_H^{0.07} \; F_{CB}^{0} \tag{2}$$

where *C* is the conversion, and NB, TB, CB, and H indicate *n*-butane, *trans*-2-butene, *cis*-2-butene, and hydrogen. We considered an average size, *L*, of our device as the aperture size in a model of two parallel and completely flat surfaces. In Knudsen diffusion, *F* is approximately proportional to L^{-1}, and in Poiseuille flow, *F* is proportional to L^{-3}. From Eqs. (1) and (2) we therefore deduce that C_{NB} and C_{TB} increase with decreasing *L*, and this dependency is much larger for C_{NB} than for C_{TB}. When an electric voltage is used to decrease *L*, the conversion of *cis*-2-butene to *n*-butane and *trans*-2-butene are affected differently. When *L* is varied, *F* is inversely proportional to the permeation rate in both Poiseuille flow and Knudsen diffusion. Therefore, from Eqs. (1) and (2) we obtain:

$$C_{NB} = k_3 \; Q_H^{-0.5} \; Q_{CB}^{0} \tag{3}$$

$$C_{TB} = k_4 \; Q_H^{-0.07} \; Q_{CB}^{0} \tag{4}$$

where *Q* is the permeation rate. Figure 3 shows that C_{NB} is proportional to $Q_H^{-0.64}$ and C_{TB} is proportional to $Q_H^{-0.17}$. On the basis of the previous results of these reactions over Pd, the behavior of the changes of the reaction rates and the permeation rates by electric fields were successfully explained from the concept of the field-induced aperture change. Moreover, we observed that switching the polarity of the electric voltage yielded almost the same result, which excludes a mechanism resulting from electrolytic reactions.

This is the first demonstration that catalytic selectivity and conversion are directly affected by a field-induced aperture change. Although the space between the two surfaces with asperities is not uniform, the measured values were reproducible because the interface contains on the order of 10^{10} asperities. This new system can be a model for a real-time, active control of pore size in catalytic reactions.

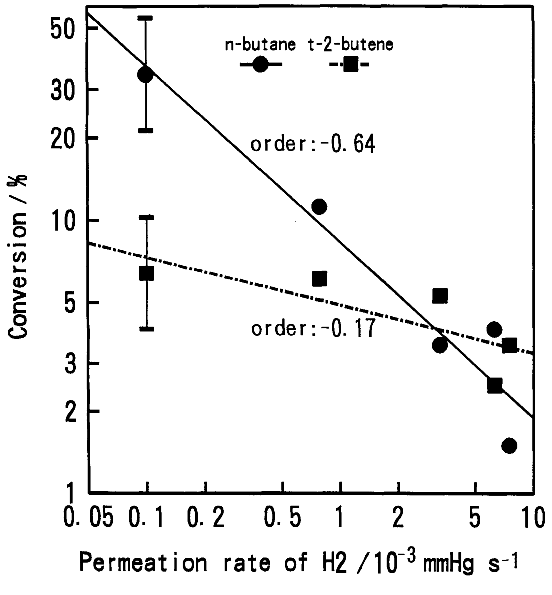

Figure 3. Conversion to *n*-butane (●) and *t*-2-butene (■) as a function of the permeation rate of hydrogen.

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