Anomalous Enhancement of the Catalytic Activity of Ferroelectrics-combined Palladium by Resonance Oscillations

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The resonance oscillations of ferroelectric lead strontium zirconium titanate and lithium niobate substrates give rise to 250–300-fold increases in the activity for ethanol oxidation of a deposited thin film Pd catalyst.

Heterogeneous catalysts have been widely used to promote chemical reactions. The attempts so far employed to enhance the functions of heterogeneous catalysis are to modify the electronic and geometric properties of the catalysts by preparation methods such as the addition of different chemical components and changes in crystalline sizes. For the development of advanced catalysts, it is desirable to design heterogeneous catalysts having artificially controllable functions that bring about a high catalytic activity and a change in selectivity *in situ* according to a given signal. Recently, we have employed surface acoustic waves, which propagate on ferroelectric $LiNbO_3$ and $LiTaO_3$ substrates, giving rise to the lattice displacement in a artificial manner.[1–5] Very recently, we have applied lattice distortion, which occurs in the ferroelectric substrate at a resonance frequency.[6]

In the present study, we have discovered that the resonance oscillations generated by low-frequency voltages of the ferroelectric substrates lead to several hundred fold activation of a deposited Pd catalyst.

Two types of poled ferroelectric crystals were employed. One was a polycrystal $Pb_{0.95}Sr_{0.05}Zr_{0.53}Ti_{0.47}O_3$ (referred to as PSZT) with a Curie temperature of 593 K. The sample was prepared in the form of a disc 0.2 mm in thickness and 20 mm in diameter. This sample provided a radial-extensional oscillation at a resonance frequency of 82 kHz. Both sides of the disk planes were covered with thick Ag electrodes. Another ferroelectrics is a 128° Y-cut lithium niobate ($LiNbO_3$) single crystal 0.5 mm in thickness, 40 mm in length and 12 mm in width. This has a length-extensional oscillation at a resonance frequency of 66 kHz. Both sides of the crystal planes were covered with Al electrodes. A catalytically active Pd metal was evaporated in vacuum by resistance-heating and deposited at a thickness of 50 nm on the Ag or Al electrodes. Low frequency (LF) voltage was generated with a function generator (HP 8116A), amplified (NF Electronic Instruments 4005S), and then applied to the electrodes in the range of a few watts.

A method of measuring the temperature of the catalyst was different from that employed in the previous study[6] in which a CA thermocouple was attached to the disc surface by Ag paste and then thick silicon resin was used to completely cover the paste to avoid exposure to the reactant gases. The disadvantage of the method making use of contact with a thermocouple was that free oscillation of the ferroelectric substrate in a resonance mode was suppressed to a large extent. In the present work, the CA thermocouple was removed so as to generate effective resonance oscillations, and a non-contacting method using a radiation thermometer detecting emission from the surface was employed for measurement of the temperatures. A reaction cell equipped with a silicon window was used for this purpose and the temperature was controlled by an outside electric furnace. Ethanol oxidation was carried out in a gas-circulating reaction system, and the products were analysed by GC connected to the reaction system. The ratio of catalytic activity with LF voltage-on to LF voltage-off, r_{on}/r_{off}, was taken as a measure of catalyst-activation efficiency.

Fig. 1 shows the ethanol oxidation at 353 K on a Pd/PSZT catalyst. When acetaldehyde formation proceeds at a steady state reaction rate, a LF voltage of 10 V was applied at a resonance frequency of 82 kHz. A dramatic rise in the reaction rate of acetaldehyde production occurred immediately. There were no significant increases at frequency other than the resonance oscillation. The LF voltage-on produced acetic acid and ethyl acetate which were not observed in the gas phase with the voltage-off: their reaction rates were $< 1\%$ that of acetaldehyde. A value of r_{on}/r_{off} for acetaldehyde formation amounted to as high as 250 in an initial stage of the voltage-on. The high activity was maintained while the voltage was being applied, and then returned to the original level after the voltage was turned off. The reaction rate of acetaldehyde formation fell as the LF voltage was applied. This is not due to the deteriorations of the Pd catalyst and the PSZT characteristics, since similar activation with the LF voltage-on occurred in the second run which was carried out after evacuation of the remaining gaseous components and then introduction of fresh reactants. It is likely that the lowering of the reaction rate results from interfering adsorption of the by-products such as water, acetic acid and/or ethyl acetate on the catalyst surface.

The radiation thermometer showed that temperature of the Pd surface rose by 20 K upon the application of LF voltage and returned to the original level in 10 min by the action of the temperature control system. This temperature rise is calculated to cause merely 2.2-fold increase in the activity, since the activation energy of ethanol oxidation on a thin film Pd catalyst[6] was reported to be 42 kJ mol^{-1}. Thus, the contribution of a thermal effect to the enhancement of the activity is less than 1% in the initial stage of the LF voltage-on.

The efficiency of activation with the LF voltage-on was strongly dependent on the conditions of the metal catalysts. Furthermore, a negligible increase in the reaction rate occurred for Pd-free PSZT at 343 K under the resonance oscillation in the range of 7–10 V. These facts eliminate the possibility that a

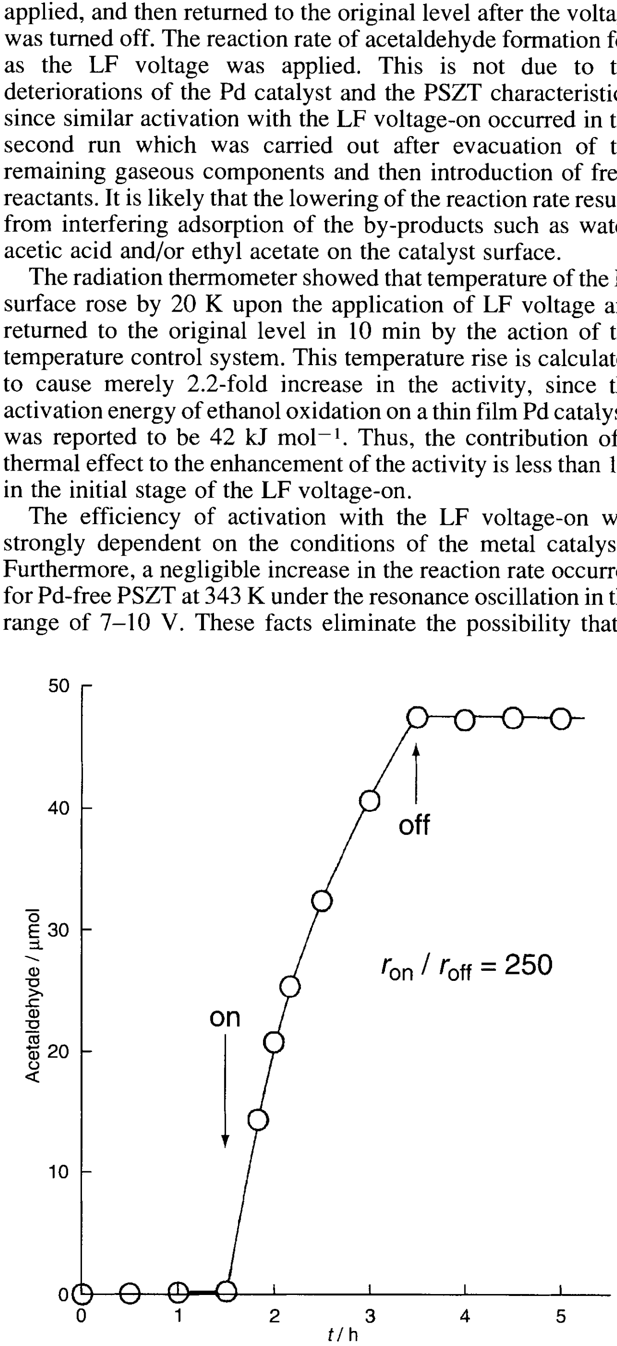

Fig. 1 Effect of resonance oscillation on ethanol oxidation over a Pd/PSZT catalyst at 10 V, 353 K, 82 kHz

homogeneous gas-phase reaction proceeds by the effects of ultrasound produced under the resonance oscillations of the substrates. For activity enhancements, one might argue the improvement of diffusion and mixing ratio of gaseous oxygen and ethanol at the gas–solid interface by the vibration of the catalyst at the resonance oscillations. However, there was no obvious indication that the reaction is controlled by diffusion. The differences in the reaction orders which were first order in the ethanol pressure and 0.55 in the oxygen pressure for ethanol oxidation over Pd[4] are too small to cause 250–690-fold increases in the catalytic activity by changes in the mixing ratio. Furthermore, the molecular masses of both gases are similar, and it is very unlikely that the mixing ratio varies significantly. From these considerations, it is concluded that remarkable enhancements in the catalytic activity are based on intrinsic surface phenomena.

A $LiNbO_3$ single crystal with a length extensional mode was used as a substrate in a Pd/$LiNbO_3$ catalyst instead of the polycrystal PSZT. A catalytic activity at a reaction temperature of 323 K increased 300-fold under a resonance oscillation of 66 kHz at a voltage of 60 V.

The radial and length extensional modes under the resonance oscillations cause a large time-dependent lattice displacement of the catalysts combined with the ferroelectric substrates. This is likely to have an influence upon electronic states, lattice vibrational modes, and local density of electrons at the surface as well as to produce interactions between sound and electrons in the catalysts; thus these phenomena are associated with a remarkable activation of the catalyst surfaces.

This work was supported by Iketani Science and Technology Foundation.

Received, 31st March 1995; Com. 5/02032H

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