pulses for excitation and they may have observed a different initial species.

We also measured the relaxation time of vibrationally hot $Cr(CO)_5$ in THF at 622 and 680 nm. It was expected that the data at 680 nm would show a faster decay than at 622 nm because, at 680 nm, one probes those molecules that are vibrationally hotter by 1370 cm^{-1}. Indeed, a 9-ps decay at 622 nm and a 4-ps decay at 680 nm were observed (Figure 3). The decay in THF at 622 nm is faster compared to cyclohexane at the same wavelength. This may be because the absorption maximum in THF appears in the bluer region compared with cyclohexane (450 nm for THF and 500 nm for cyclohexane). Therefore, $Cr(CO)_5(THF)$ is vibrationally hotter (2220 cm^{-1}) than $Cr(CO)_5$(cyclohexane) at 622 nm.

Our data indicate that the dynamics for solvation in the highly reactive pentacarbonyls is controlled by the dissipation of the excess vibrational energy to surroundings. The intermolecular energy transfer times of vibrationally hot $Cr(CO)_5$ in cyclohexane and THF appear to be 4–21 ps for the excess energy of 4000–7500 cm^{-1}, which are faster than T_1 relaxation times of the CO stretching in $Cr(CO)_6$ in solution as measured by Heilweil et al.[10] Our observation of vibrational cooling, we think, may clarify the issue of the existence of "naked" $Cr(CO)_5$ in liquids.

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Effect of Surface Acoustic Wave Generated on Ferroelectric Support upon Catalysis

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The development of a catalyst whose function can be activated by external energy is one of the most interesting subjects. We have directed our attention to the surface acoustic wave (SAW) which can be propagated on ferro- and piezoelectric crystals having no center of symmetry.[1-3] Since the wave is able to cause the replacement of lattice atoms and an associated electric field, it would be expected that the SAW possesses the capability of activating a catalytic phase combined with a ferroelectric surface. There have so far been few studies on the effect of the SAW in this respect, and, to our knowledge, this is the first report describing the availability of the SAW for catalysis.

In the present work, a SAW was generated on a ferroelectric $LiNbO_3$ substrate which had a high piezoelectric coupling coefficient. Palladium was chosen as a catalytically active phase and was deposited as a thin film on the ferroelectric substrate.

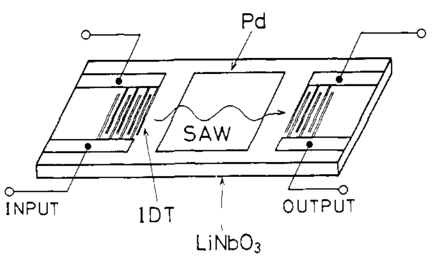

Figure 1. Schematic representation of a SAW catalyst.

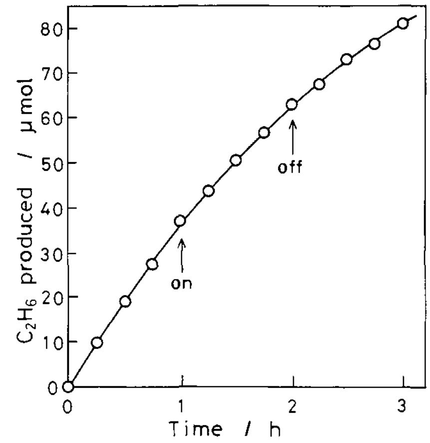

Figure 2. Hydrogenation of C_2H_4 on a SAW catalyst. Initial pressures: 4 kPa of H_2 and C_2H_4.

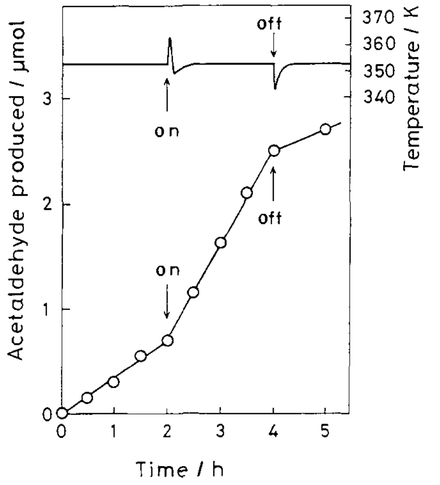

Figure 3. Effect of a SAW upon the catalytic activity of Pd for the formation of acetaldehyde and temperature of the catalyst surface. Initial pressures: 4 kPa of C_2H_5OH and O_2.

A SAW device employed is schematically shown in Figure 1. The interdigital transducer (IDT) electrodes were fabricated photolithographically at each end of a polished single-crystal surface of 128°-rotated Y-cut $LiNbO_3$. The electrode for SAW generation had 20 pairs of a double finger with a spacing of 200 μm, and the SAW-receiving electrode had the same structure except for 14 pairs. Both the electrodes consisted of a 10-nm underlying Cr layer covered with an inactive 100-nm-thick Au layer. The distance between the SAW generation and detection electrodes was 16 mm, in the middle of which a Pd film was deposited at a thickness of 10 nm by evaporation with resistance heating. Radio frequency (rf) power was generated from a network analyzer, then amplified, and, after adjustments through several attenuators, applied at 1 W. The electric circuit was set up so that the SAW was able to pass through the Pd catalyst and then to return back to the network analyzer.

The gas-phase catalytic reactions were investigated in a high-vacuum circulating system in which the Pd-incorporated SAW catalyst was placed in a quartz reaction cell with the electrodes. The temperature of the catalyst was monitored by a small thermocouple connected directly to the back of the $LiNbO_3$ substrate and held constant with an outside electric furnace. It was experimentally confirmed that changes in the temperature of the Pd surface were reflected in the back of $LiNbO_3$ substrate with a delay of ca. 10 s. This delay was negligibly small, compared to the scale of time during which the catalytic reactions were being examined.

The bandpass characteristics of the SAW device showed that the center of the SAW appeared at a frequency of 19.5 MHz and

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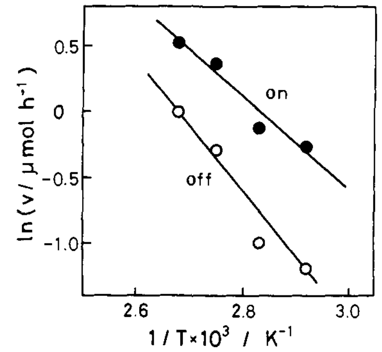

Figure 4. Temperature dependence of C_2H_5OH oxidation: ○, SAW-off; ●, SAW-on.

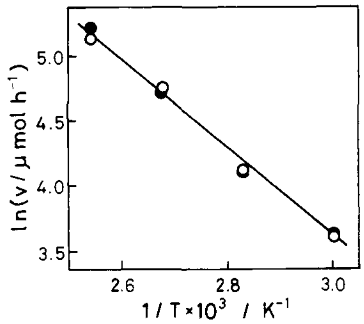

Figure 5. Temperature dependence of C_2H_4 hydrogenation: ○, SAW-off; ●, SAW-on.

its bandwidth was 1.5 MHz at an attenuation of 10 dB. The center frequency was consistent with the value expected from the space between the finger electrodes.

Figure 2 shows the results on the catalytic hydrogenation of ethylene at 333 K. The relationship between the production of ethane and reaction time shows a slightly downward curve because of a gradual decrease in the catalytic activity as the reaction proceeds. Nevertheless, it is obvious that there were no significant changes in ethane production when the SAW was turned on and off. In the reaction of C_2H_5OH with O_2 at 353 K, acetaldehyde is mainly produced. Figure 3 shows that when the SAW was turned on (SAW-on), an immediate increase in the production of acetaldehyde took place; the activity became ca. 2.6 times larger than that in the absence of the SAW (SAW-off). With SAW-off, the activity decreased nearly to the original level before SAW-on. The SAW propagation at rf power will apparently result in the generation of heat on the catalyst, and one might argue about a temperature rise at the catalyst surface. In fact, the temperature of the SAW catalyst measured increased to 363 K immediately after the SAW application. As shown in Figure 3, however, the temperature sharply decreased as a consequence of control by the surrounding electric furnace. After fluctuations, the original level of the temperature was recovered within less than 20 min, whereas the production of acetaldehyde with a higher rate continued over a period of longer than 2 h until the SAW was turned off.

Figure 4 shows the temperature dependence of the oxidation of C_2H_5OH. Without the SAW, the activation energy was evaluated to be 42 kJ mol^{-1}, whereas it decreased to 29 kJ mol^{-1} under the conditions of SAW-on. The distinct differences in the activation energy demonstrate that the SAW is able to give a noteworthy influence to the kinetic behavior of the reaction. As shown in Figure 5, on the other hand, there was no significant change in the activation energy for the hydrogenation of C_2H_4 between SAW-on and SAW-off. It is to be noted that the hydrogenation exhibits no activity increases by the SAW, irrespective of its positive activation energy of 27 kJ mol^{-1}. The comparison of temperature dependence in the two reactions indicates that the presence or absence of a SAW effect is dependent upon the kinds of catalytic reactions. From the above-mentioned findings, it is rational to conclude that the activity enhancements are not due to a thermal effect but to one of SAW-inherent phenomena.

In the previous study, poled ferroelectric $LiNbO_3$ having a polarization axis perpendicular to the surface was used as a catalyst support on which the catalytically active phases such as Pd[4] and NiO[5] were deposited, and it was shown that the activation energy of CO oxidation varied according to the direction of the polarization axis. This polarization effect is associated with a static electric field of the underlying ferroelectric surface. The effect of the SAW observed in this study is ascribable to a dynamic behavior; either or both of the displacement of lattice atoms and the fluctuations of an electric field resulting from the surface wave seem to be responsible for the activation of the Pd surface. One of the interesting features is that the SAW is likely to be effective for the reaction involving a polar molecule.

The present study clearly demonstrates that the SAW has a high potential to develop a device-type catalyst whose catalytic activity can be controlled by an external signal. Further study is in progress.

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Reaction of In(t-Bu)$_3$ with Dioxygen: Synthesis and Molecular Structure of [(t-Bu)$_2$In(OO-t-Bu)]$_2$

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The autoxidation reactions of group 13 organometallic compounds (MR_3, M = B, Al, Ga, In) are usually uncontrollably fast; lower alkyl derivatives often inflame spontaneously in air, while higher alkyl derivatives, with lower vapor pressures, may char but not ignite. If the supply of oxygen is restricted, a smooth reaction takes place, to yield the alkoxide compounds via alkylperoxo intermediates (eq 1).[1-3] In the case of boron, many of the intermediate peroxides can be isolated, usually as rather unstable oils.[4] Although proposed in a number of studies,[5] no examples of the heavier group 13 analogues of these boron alkyl peroxides have been isolated. We report here the synthesis and structural characterization of the first stable (alkylperoxo)indium compound.

$$\text{M-R} \xrightarrow{O_2} [\text{M-OOR}] \rightarrow \text{M-OR} \qquad (1)$$

The interaction of In(t-Bu)$_3$[6] with an excess (1 atm) of dry oxygen leads to the formation of the alkylperoxo compound (t-Bu)$_2$In(OO-t-Bu) (**1**) (eq 2).[7] Compound **1** may also be prepared, albeit in low yield, by the reaction of In(t-Bu)$_3$ with pyridine

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(7) A yellow solution of In(t-Bu)$_3$ (1.00 g, 3.50 mmol) in pentane (50 mL) was cooled to 0 °C. Dry O_2 was bubbled through the solution until the solution became colorless, <1 min. The solvent was removed under vacuum, yielding a white crystalline solid, which can be recrystallized from pentane (-20 °C). Yield: 60-70%. ^{1}H NMR (δ ppm, C_6D_6): 1.49 (s, 18 H, In-t-Bu), 1.15 (s, 9 H, OO-t-Bu).

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