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A Catalytic Reaction on Alumina Studied by Tunneling Spectroscopy: Transfer Hydrogenation of Muconic Acid[1]

DUNCAN E. MCBRIDE[2] AND JAMES T. HALL[3]

Department of Physics, University of California, Santa Barbara, California 93106

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Tunneling spectroscopy is a sensitive method for studying the catalytic properties of alumina which grows thermally on an aluminum strip. We observe controlled catalytically induced transfer hydrogenation from water vapor of muconic acid, a conjugated hydrocarbon chain chemisorbed on the alumina with carboxylate groups at both ends. Between 25 and 400°C the amount of hydrogen transferred grows exponentially with temperature; in the range of parameters accessible to us the reaction is time independent and only weakly pressure dependent. Hydrogen is transferred from the water vapor through hydroxyl groups on the surface. The reaction does not go to completion at a fixed temperature because it runs out of available surface hydrogen.

INTRODUCTION

Alumina (aluminum oxide) is a common support material for industrial catalysts, and there is substantial evidence that the alumina plays an active role in their operation (*1*). In addition, alumina, alone or in an alumina–silica mixture, is a catalyst in some reactions. Hansma *et al.* (*2*) have shown that the oxide that grows naturally on a freshly evaporated aluminum surface is similar physically, chemically, and catalytically to commercial γ-alumina. Such an oxide is formed during the fabrication of a tunnel junction used in inelastic electron tunnelling spectroscopy. Thus, reactions that occur on the oxidized aluminum electrode of a tunnel junction are relevant to the study of catalysis, and reactants, products, and intermediates in such reactions can be observed with the great sensitivity of tunneling spectroscopy.

Inelastic electron tunneling spectroscopy reveals the vibrational spectrum of organic molecules on the oxide of a metal-oxide–metal junction (*3*). A vibrational mode of frequency ν appears in the tunneling spectrum as a peak in the second derivative of voltage with respect to current, d^2V/dI^2, at a voltage $V = h\nu/e$ (where h is Planck's constant, and e is the electron charge). Both infrared and Raman active modes can be observed. Tunneling spectroscopy can be used to observe a small fraction of a monolayer of molecules, although about one monolayer is optimum (*4*).

We report here the observation of controlled, catalytically induced transfer hydrogenation from water vapor of an unsaturated hydrocarbon chain chemisorbed to the alumina at both ends of the chain. The temperature of the substrate primarily controls the amount of hydrogena-

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[2] On leave from Department of Physics, Swarthmore College, Swarthmore, Pennsylvania 19081.

[3] Present Address: National Bureau of Standards, Washington, D. C. 20234.

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tion; in the range of parameters accessible to us, reaction time and water vapor pressure play lesser roles.

To our knowledge this is the first use of tunneling spectroscopy to study a reaction which has been controlled by varying external parameters and in which intermediate stages have been observed. Using tunneling spectroscopy it should be possible to study other such catalytic reactions on an alumina surface.

EXPERIMENT

Junction fabrication. Based on previous work by Hall and Hansma (*5*), we chose muconic acid (*trans*, *trans*-1,3 butadiene 1,4-dicarboxylic acid, HOOC–CH=CH–CH=CH–COOH) for our study. It is the shortest chain dicarboxylic acid which includes conjugated double bonds. In addition, for comparison we used the saturated analog, adipic acid (1,4-butanedicarboxylic acid, $HOOC–(CH_2)_4–COOH$). Both acids were obtained from the Aldrich Chemical Co. and used without further purification. As a solvent for the acids we used Spectroquality methanol obtained from Matheson, Coleman, and Bell.

We fabricated tunnel junctions in a standard way previously described in detail (*3*). In outline, (a) in high vacuum we evaporated an aluminum strip 1500 Å thick and 1 mm wide onto a clean 1 × 3-in. glass microscope slide at room temperature, (b) oxidized the strip in air to form a thin ($\cong$20 Å) alumina layer, (c) doped the partially oxidized aluminum strips with a 1-g/liter acid solution, (d) heated the doped strip in water vapor to a temperature of interest by the technique described in the following section, and (e) completed the junction with a cross strip of lead 3000 Å thick and 1 mm wide. We used 99.999% purity aluminum and lead obtained from Alfa Products, Ventron Corp.

Heating technique. To heat the strip we used a modification of the technique developed by Bowser and Weinberg (*6*). Before junction fabrication we evaporated an aluminum heating strip, whose dimensions were identical to the junction strip, onto the back of the slide opposite the area where the junctions would be located. This strip terminated in four pads, to which electrical contacts could be made. We annealed the strip in atmosphere at 200°C for 10 min, soldered indium contacts on the pads, and put the slide into the evaporator for the standard junction fabrication. After doping the junction strip as described previously, we attached fine wires to the electrical contacts of the heating strip and replaced the slide in the vacuum chamber for heating and completion of the tunnel junction.

Before heating we pumped the vacuum chamber to 10^{-5} Torr and isolated it from the pump. We then opened a valve leading to a glass bulb containing liquid water and allowed the pressure to rise to the desired value, usually 0.3 Torr. We used deionized distilled water, H_2O, produced in our laboratory or 99.8% isotopically pure heavy water, D_2O, obtained from Stohler Isotope Chemicals. Since the walls of the vacuum system adsorbed water rapidly, it was necessary to open the valve periodically to keep the pressure up to the desired value.

As soon as the proper pressure was reached, heating began. We passed a set current through the heating strip and monitored the voltage across it to determine its resistance. To determine the strip temperature we used the relation [Eq. (2) of Ref. (*6*)]

$$\Delta T = 1/b \frac{\Delta R}{R_i},$$

where ΔT is the change in temperature from the reference, room temperature, ΔR is the change in resistance from the initial value, R_i, and b is the temperature coefficient of resistance of the heating strip. To determine b we had previously measured (in a vacuum oven) the temperature coeffi-

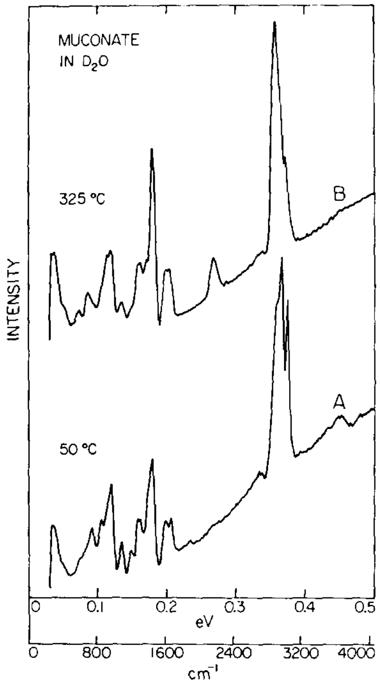

FIG. 1. Spectra of two muconic-acid-doped junctions. After doping, the oxidized aluminum strips were heated in 0.3 Torr of D_2O vapor, the strip in trace A to 50°C and the strip in trace B to 325°C.

cient of a set of films made in our evaporator. In agreement with Bowser and Weinberg (*6*) the coefficient varies about 10% from sample to sample made under similar conditions. Thus the temperatures we report are accurate to about 10%.

At the end of the heating period we allowed the strips to cool for about 1 min in the vapor and then opened the pump. Since only the glass slide was heated, it cooled rapidly to about 25 to 30°C during the time (about 8 min) it took to reduce the pressure low enough (5×10^{-6} Torr) to complete the junction with cross strips of lead.

We heated an auxiliary strip on the back of the slide rather than the strip used to make the junctions for two reasons. First, there was less evidence of contamination from the process of attaching the leads to the strip. Second, the geometry of our evaporator made it difficult to attach leads to the front of the slide. The fact that we measured the temperature of the heating strip and not that of the sample strip did not cause appreciable error in our experiments. We simultaneously measured both strip resistances on a sample slide and determined that even with rapid heating the indirectly heated strip reached an equilibrium temperature only 15 to 30 sec after the directly heated one, and its equilibrium temperature was roughly 5% lower than that of the heated strip. Since we held the stated temperature for 3 min or more, the few seconds time lag is unimportant, and we have corrected for the small temperature difference in our reported values.

Tunneling spectra. We checked the room temperature resistance of the completed aluminum–alumina–dopant–lead junctions with a low-power ohmmeter (7). The resistances were usually two to three orders of magnitude higher than an undoped, heated control junction. We then attached electrical leads to the junction strips and immersed the assembly into liquid helium at 4.2 K to check for proper current–voltage characteristics to ensure that all the current was due to tunneling (*8*).

We obtained second-derivative spectra by using a lock-in amplifier to measure the second harmonic voltage due to a small modulation current as a function of voltage over the range 0.05 to 0.5 V (corresponding to photon wavenumbers of about 400 to 4000 cm^{-1}). Experimental details of tunneling spectroscopy have been described previously (*3*).

RESULTS

Spectra

Figure 1 shows spectra from two junctions whose aluminum strips had been doped with muconic acid and heated to different temperatures in an atmosphere of 0.3 Torr of heavy water vapor (D_2O). Spectrum A is of a junction heated to 50°C and is indistinguishable from spectra obtained from junctions fabricated entirely at room temperature. Spectrum B was obtained from a junction whose aluminum strip had been heated to 325°C for 3 min. We used heavy water to hydrogenate the acid in order to distinguish between added hydrogen and the hydrogen already on the hydrocarbon. Between the two spectra all the peaks change to some extent. The most notable changes are the appearance of a peak at 267 mV (2150 cm^{-1}) and substantial reduction in the size of the peaks at 333 (2685 cm^{-1}), 374 (3015 cm^{-1}), and 450 mV (3630 cm^{-1}). Under our experimental conditions the relative intensities of peaks from identically prepared samples were reproducible within 10% in all cases. The changes we note in samples prepared at different temperatures are much larger.

Chemisorption of Muconic Acid on Alumina

From the tunneling spectrum shown in Fig. 1, spectrum A, we can determine that the dicarboxylic acid, muconic acid, loses two protons from the acid groups and chemisorbs on alumina as a dianion. Instead of a carbon–oxygen double bond stretch mode near 1690 cm^{-1} that is characteristic of an associated muconic acid (*9*), symmetric and antisymmetric carboxylate stretch modes appear near 1450 and 1590 cm^{-1} which are characteristic of carboxylate groups with equivalent oxygens chemisorbed on alumina (*5*). Similar carboxylate stretch mode positions have been found for monocarboxylic acids chemisorbed on alumina as symmetric, bidentate monocarboxylate anions (*5*). Therefore, the muconic acid chemisorbs on alumina at room temperature as muconate, $O_2^-C{-}CH{=}CH{-}CH{=}CH{-}CO_2^-$. Vibrational modes associated with the carbon–carbon double bond stretch (*10*), ν(C=C), and the carbon-hydrogen stretch mode (*10*), ν(=C–H), appear as peaks near 1660 and 3015 cm^{-1}. These and other peaks are characteristic of the *trans, trans*-muconate structure (*9*). Because of its planar structure, the molecule must lie flat on the alumina surface. We note that tunneling theory (*3*) and experiments (*5, 5a*) show that excitations of substantial intensity are possible for molecules with dipoles flat on the surface.

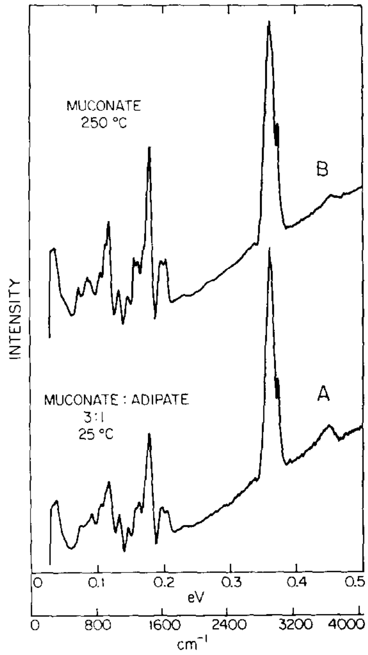

FIG. 2. A. Spectrum of an unheated junction doped with a 3 to 1 mixture of muconic to adipic acids, 1 g/liter in methanol. B. Spectrum of a junction whose muconic-acid-doped aluminum strip was heated to 250°C in 0.3 Torr of H_2O vapor. The size of the 3015-cm^{-1} ν(=C–H) peak is approximately the same in both traces.

Hydrogenation of Muconate on Alumina

The peak which appears at 2150 cm^{-1} is characteristic of a carbon–deuterium stretch mode (*11*), ν(C–D). We interpret its appearance and the substantial decrease in intensity of the ν(=C–H) peak on heating to mean that some of the unsaturated carbons in the muconate surface species are gaining a deuterium atom. (The be-

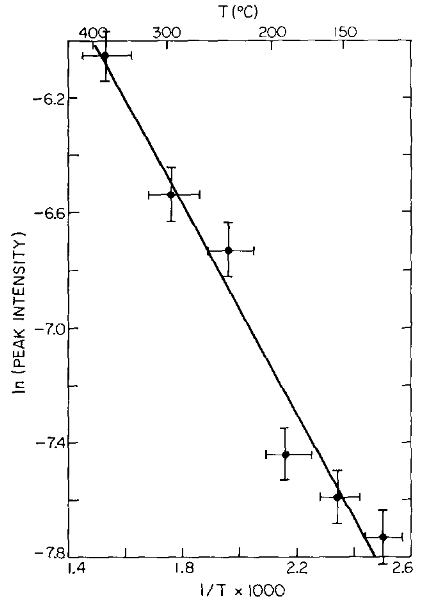

FIG. 3. Temperature dependence of the 2150-cm^{-1} ν(C–D) peak for junctions made on a muconic-acid-doped, heated aluminum strip. Peak intensity is expressed as the fractional change in the junction resistance due to the mode. The line is a linear least square fit to the points, which indicate the measured temperatures and the mean peak intensity for the experiments at each temperature.

havior of the ν(C=C) peak cannot be determined unambiguously in muconate since it cannot be clearly separated from the broad antisymmetric carboxylate stretch peak at 1590 cm^{-1}.) The source of the deuterium atoms must be the D_2O vapor, and we show in the next section that intermediate between the vapor and the hydrogenated compound is a deuteroxyl group on the alumina surface. The alumina is a catalyst in the process.

To determine the reaction product we doped junctions with solutions containing varying proportions of muconic and adipic acids. As shown in Fig. 2, a mixture of muconic to adipic acids 3 to 1 doped at room temperature reproduces quite closely the spectrum of muconate heated to 250°C in H_2O. Most importantly, the ν(=C–H) peak is approximately the same size. Other proportions, such as 1 to 1, 2 to 1, or 4 to 1 had a peak clearly too large or too small. Since the proportion actually sticking to the alumina is unknown, the exact proportion in solution is unimportant. However, the experiment indicates[4] that the end product of heating muconate on alumina is adipate, $O_2^-C-(CH_2)_4-CO_2^-$.

The spectrum shown in Fig. 2, spectrum B, also eliminates the possibility that the effect of heating muconate shown in Fig. 1 is due merely to hydrogen–deuterium exchange. Such an exchange would result in an increase in the ν(C–D) peak and a decrease in the ν(=C–H) peak. However, the ν(=C–H) peak in Fig. 2, spectrum B, is of the same intensity as if the strip had been heated in D_2O vapor. If there had been only hydrogen–hydrogen exchange, we would have expected no change in the spectrum from that obtained at room temperature.

We have heated muconate on alumina in D_2O vapor to other temperatures between room temperature and 400°C. The intensity of the ν(C–D) peak grows as the temperature is raised. Figure 3 shows this behavior. Although Fig. 3 is in the form of an Arrhenius plot, we note that the quantity on the abscissa is not a rate but a peak intensity. The intensity is independent of time over the range 3 to 35 min; for significantly shorter times we cannot be sure the junction strip reaches the temperature of the heating strip. We discuss the implications of this behavior in the Discussion section. There is a small dependence of the ν(C–D) peak intensity on D_2O vapor pressure: For a temperature of 250°C the peak intensity is about 50% greater at 15 Torr than at 0.3 Torr.

There may be some hydrogenation of

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[4] The other candidate, hydromuconate, $O_2^-C-CH_2-CH=CH-CH_2-CO_2^-$ has a ν(=C–H) peak intensity larger than that of muconate. Since we observe a ν(=C–H) peak intensity decrease on heating, the product cannot be hydromuconate.

muconate immediately upon doping the junction, since a peak at 2950 cm^{-1} due to alkyl hydrogen appears even in spectra from junctions made at room temperature. However, we start with the same amount of muconate on the surface in each experiment, and our reactions are carried out on that muconate.

We have also heated adipate on alumina in D_2O vapor to a number of temperatures. There is neither any appearance of a ν(C–D) peak nor a decrease in any other peak in its spectrum.

Finally, we attempted to use deuterium gas to hydrogenate the muconate on alumina. Under similar conditions of temperature and pressure we observed neither ν(C–D) nor ν(O–D) peaks.

Transfer Hydrogenation from Surface Hydroxyl Groups

How does the hydrogen get from the water vapor onto the muconate? To answer this question we examine the behavior of the hydroxyl surface species.

A peak due to hydroxyl groups is present in the background spectra of all tunneling junctions fabricated at room temperature. The oxygen–hydrogen stretching mode (*12*), ν(O–H), appears as a broad peak centered at about 3630 cm^{-1} (450 mV). Further, the hydroxyl groups readily exchange to deuteroxyl groups at room temperature when D_2O vapor is admitted into the vacuum system (*13*).[5] Hydroxyl and deuteroxyl stretch modes ν(O–H) and ν(O–D) appear in Fig. 1, spectrum A at 3630 and 2685 cm^{-1}, respectively. However, no such modes appear in Fig. 1, spectrum B, and they appear only weakly, if at all, in any spectrum of a junction made with muconic acid and heated above about 125°C.

We see no decrease in the hydroxyl peak in heated, undoped junctions. This behavior strongly suggests that the hydroxyl and deuteroxyl groups react with the unsaturated bonds in muconate to saturate them. Also, the reaction apparently modifies the surface, since it does not rehydrate as readily as we would expect in the vacuum chamber, where the residual pressure of 5×10^{-6} is largely water vapor.

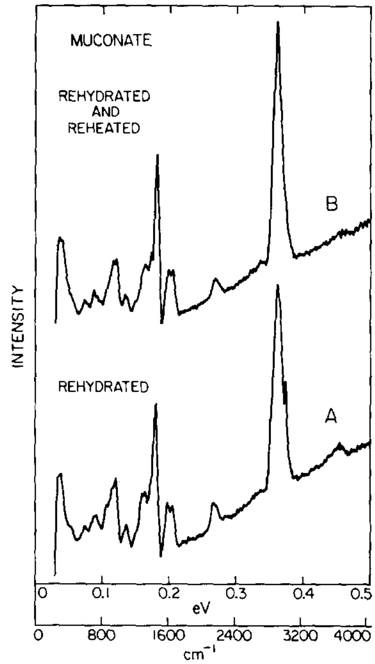

FIG. 4. A. Spectrum of a junction doped with muconic acid whose oxidized aluminum strip was heated to 250°C in 0.3 Torr of D_2O vapor, cooled, and exposed to room air of 50% relative humidity before completion. Note the return of the 3630-cm^{-1} ν(O–H) peak compared to Fig. 1, spectrum B. B. Same as A, except the strip was heated in H_2O, rehydrated, and reheated in D_2O. A prominent ν(C–D) peak appears, and the ν(=C–H) and ν(O–H) peaks are substantially reduced, compared to A.

However, the heated surface of muconate on alumina can be rehydrated at higher pressure. After heating a doped sample to 250°C in D_2O and cooling it, but prior to evaporating the lead cross strip, we exposed the surface to atmospheric pressure of room air with 50% relative humidity. In addition to the usual spectrum, including a ν(C–D) peak, there appeared a ν(O–H)

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[5] Under our experimental conditions we could not quite exchange all the hydroxyls to deuteroxyls, but our results were reproducible.

peak almost as intense as if the surface had not lost its hydroxyl groups (Fig. 4, spectrum A).

This rehydrated surface can be used for further hydrogenation of unreacted muconate. In a successive experiment we heated the doped surface in H_2O vapor, rehydrated it, and then heated it again in D_2O vapor. The spectrum showed a normal ν(C–D) peak (from the second heating) and no ν(O–D) peak. Further, the spectrum had a much smaller ν(=C–H) peak than would be expected from a single heating (Fig. 4, spectrum B).

Thus the hydroxyl or deuteroxyl groups added after the first heating can react with some of the remaining muconate and produce more complete hydrogenation if the surface is heated again. A possible mechanism is for a surface site holding a hydroxyl group to give up a hydrogen to muconate on heating. The modified site could then be used for rehydration and further hydrogenation. The fate of the leftover oxygen ions in such a reaction is unknown to us, but we do not observe them attached to any of the surface species.

Reaction-Limiting Step

The mechanism we propose also provides a qualitative explanation for why the reaction does not go to completion under conditions available to us: It runs out of a surface source of hydrogen. For reasons unknown to us the surface rehydrates with difficulty at lower pressure after heating. Increasing the temperature provides a larger supply of hydroxyl groups, but never a continuous one. Since the reaction is irreversible, Fig. 3 shows that the reaction proceeds to a point determined by the temperature and stops. The most likely reason for this behavior is that it runs out of a reactant, hydrogen.

DISCUSSION

Other researchers have reported the catalytic hydrogenation of the unsaturated hydrocarbon, ethylene, over a dehydrated alumina using hydrogen or deuterium gas (*14*). We found that deuterium gas would not hydrogenate muconate on alumina under our experimental conditions. Instead, we found that muconate hydrogenates on a heated, hydrated surface. To our knowledge this is the first time that water has been used as a source for transfer hydrogenation, and in particular, the first time it has been used in a catalytic reaction to hydrogenate a surface species on alumina.

It is not clear from one species alone, muconate, why it should hydrogenate in the way we observe. For example, we cannot distinguish between the effect of bond stability (resonance stabilization of this conjugated species) and the effects of important geometric parameters (proximity to the alumina surface and active sites for hydrogenation). We are beginning further work with other closely related carboxylic acids in order to explore some of these effects. In addition, the role of the carboxylate ions in the process is unknown: Are they important for the hydrogenation to occur, or do they only serve to bind the muconate flat on the surface in proximity to active sites?

We present the transfer hydrogenation of muconate as an example of what we believe is a class of catalytic reactions on alumina that can be studied with tunneling spectroscopy. We have explored this reaction in the temperature range of 25 to 400°C, and only mechanical constraints have prevented us from going higher. (Ordinary microscope slides tend to shatter when we heat them.) At least another 100°C should be possible, giving temperatures well into the range where commercial alumina catalysts are activated.

SUMMARY

Tunneling spectroscopy is a sensitive tool for studying chemical reactions on an alumina surface, and we report here the first study of a temperature-controlled catalytic reaction at high temperature on such a surface. Muconic acid chemisorbs as muconate on alumina. Upon heating, this muconate undergoes hydrogenation to adipate when heated in water vapor. Hydrogen is transferred from the water vapor through hydroxyl groups that form naturally on the alumina surface. Under conditions we used, the reaction is limited by the availability of hydroxyls on the surface. It should be possible to study other catalytic reactions using tunneling spectroscopy.

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