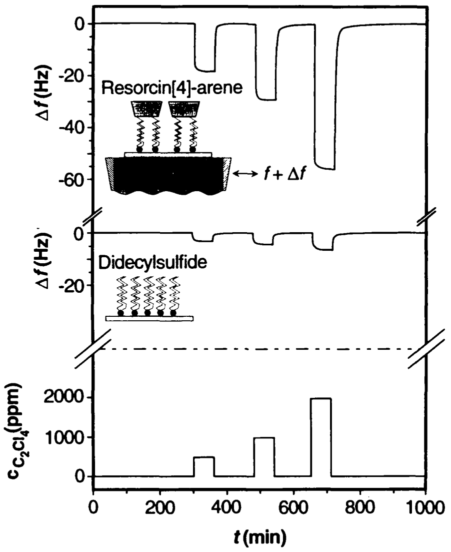

Fig. 4. Changes of frequencies Δ*f* as a function of time *t* during exposure of monolayers of resorcin[4]arene and didecylsulfide to different concentrations $c_{C_2Cl_4}$ in synthetic air at $T = 303$ K. For simplification, the noise of the signal, ± (2 to 3) Hz (which mainly results from small fluctuations of the temperature, which affect the oscillation frequency of the quartz), is omitted here.

tions of C_2Cl_4 in the parts per million range in synthetic air (that is, N_2-O_2 mixtures) at a constant temperature $T = 303$ K. Typical results of the shift Δ*f* in the fundamental oscillation frequency are shown in Fig. 4. Resorcin[4]arene monolayers show a fast interaction with C_2Cl_4. Steady-state values Δ*f* are reached after short response times. Evidently, a thermodynamic equilibrium between C_2Cl_4 in the gas phase and the resorcin[4]arenes is adjusted immediately. By contrast, the interaction of C_2Cl_4 with didecylsulfide monolayers leads to relatively small changes Δ*f* under the same conditions. This may be attributed to the occupation of interstitial sites of the aliphatic chains, which results from their lipophilic properties. For comparison, we also determined Δ*f* for other organic molecules, including chloroform, trichloroethylene, and toluene, monitored at the same pressures and temperature (303 K). These results show that the resorcin[4]arenes have a high selectivity toward incorporation of C_2Cl_4 molecules, as was already indicated in the lower part of Fig. 1.

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Nanocatalysis by the Tip of a Scanning Tunneling Microscope Operating Inside a Reactor Cell

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The platinum-rhodium tip of a scanning tunneling microscope that operates inside of an atmospheric-pressure chemical reactor cell has been used to locally rehydrogenate carbonaceous fragments deposited on the (111) surface of platinum. The carbon fragments were produced by partial dehydrogenation of propylene. The reactant gas environment inside the cell consisted of pure H_2 or a 1:9 mixture of CH_3CHCH_2 and H_2 at 300 kelvin. The platinum-rhodium tip acted as a catalyst after activation by short voltage pulses. In this active state, the clusters in the area scanned by the tip were reacted away with very high spatial resolution.

The dream of surface scientists to elucidate the atomic structure of catalyst surfaces in the course of a chemical reaction in real conditions of high reactant pressures (≥ 1 atm) and temperatures (~500 K) has become possible by the recent development of a scanning tunneling microscope (STM) that operates inside a reactor cell (*1*, *2*). A logical extrapolation and refinement of this concept is to see if, in addition to atomic-resolution images, the tip of the STM can act catalytically to effect surface reactions with atomic spatial resolution. A precursor to this idea is found in the numerous experiments in which an STM tip was used to pattern a surface and manipulate atoms (*3*).

In this report, we present evidence that shows the chemical activity of an STM tip that catalyzes with high spatial resolution the rehydrogenation of carbonaceous species on the Pt(111) surface. The STM and the reactor cell used in these experiments have been described in detail (*1*). The tips were made of wires of 80% Pt and 20% Rh and had an apex radius of about 100 Å, as estimated from measurements of atomic step heights and widths. The Pt(111) substrate was prepared in a separate ultrahigh-vacuum chamber (base pressure, 10^{-10} torr) equipped with low-energy electron diffraction and auger electron spectroscopy (*4*). Once clean and ordered, the Pt surface was protected from contamination by adsorbing a sacrificial monolayer of sulfur that formed a $(\sqrt{3} \times \sqrt{3})R30°$ ordered structure [the sulfur atoms are separated by $\sqrt{3}$ times the underlying Pt–Pt distance and the sulfur unit cell is rotated 30° with respect to the Pt(111) orientation]. The sample was transferred to the reactor cell in a small transfer chamber at a pressure of 10^{-6} torr. Then we removed the protective S layer by heating it in pure oxygen at a pressure of 1 atm. The oxygen was pumped down to 10^{-5} torr, and a mixture of propylene (10%) and H_2 (90%) was admitted to the chamber with the sample at room temperature.

Propylene readily adsorbs on the surface of Pt under these conditions and forms ordered structures of propylidyne ($\equiv C-CH_2-CH_3$) (*5*). As shown by the previous STM studies of a similar molecule (ethylidyne, $\equiv C-CH_3$) by Land *et al.* (*6*), the mobility of the adsorbed molecules on the Pt(111) surface is too large at room temperature, and no atomic resolution can be obtained. The STM images show the surface consisting of flat and featureless terraces and monatomic height steps that are also characteristic of the clean Pt(111) (Fig. 1A).

We then partially decomposed the propylidyne species by heating it in a vacuum (after pumping the propylene-H_2 gas mix-

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ture or after backfilling the cell with pure CO). The amount of hydrogen lost from the surface as a result of this heating depends on the temperature and produces carbonaceous clusters as a result of the polymerization of the hydrocarbon fragments (7). After heating to 550 and 700 K in 1 atm of CO, clusters form that are 3 Å tall and have peculiar shapes that are characteristic of the decomposition temperature and of the gas environment during imaging (Fig. 1, B and C). In the presence of CO, their shape is a result of the competition for sites of CO and the hydrocarbon fragments that can be displaced reversibly upon coadsorption. The clusters have regular diameters and occupy the entire width of the Pt substrate terraces (~100 Å), forming rows parallel to the step directions. As the decomposition temperature is increased, the clusters become smaller and more compact.

To observe the tip-induced catalysis, we filled the cell with 1 atm of the propylene-H_2 mixture and maintained it at room temperature. The reaction initiated when the tip was "activated" by pulses of several tenths of a volt (Fig. 2A). In the upper third of the image, we observe the characteristic clusters formed by the previous heating of the propylene layer to 550 K, aligned with the direction of the step edges (as in Fig. 1B). A pulse applied at the position labeled "p" produced the 15 Å elevation, which indicates that material was transferred from the tip to the substrate by the pulse. Below this line, as the tip continued to scan, the clusters were removed. If the tip was immediately moved to a fresh area while it remained active, all of the clusters were again removed from the area scanned (Fig. 2B). Eventually, the activity of the tip decayed (its lifetime being on the order of minutes), presumably by contamination that prevented H_2 adsorption and dissociation at the apex (Fig. 2C).

Catalytic activity could be restored once more by additional pulses to remove contaminant material (Fig. 3). The large feature in Fig. 3A (marked "f") appears double because of a double-tip apex. Such double-tip effects are commonly observed in experiments where relatively high features are present. The remainder of the image does not exhibit the double-tip aberration because the features have much smaller corrugations. The tip was catalytically inactive during this entire image acquisition.

Immediately afterward, the tip was pulsed twice near the center of the same area, resulting in two bumps (Fig. 3B). The active tip obtained was used to image the same area as that shown in Fig. 3B. All of the clusters were removed in the top part of the image (see expanded area). Feature f was also thinned out (its height was cut in half after passage of the active tip).

The tip was suddenly turned off or deactivated at a point in the line marked by the arrows. For this reason, the clusters in the region below remained intact. This process of activation and deactivation can be repeated many times. In general, the catalytic lifetime of the tip was not dependent on the pulse duration, polarity, or magnitude. A further activation pulse again produced a very active tip that removed all clusters in the area, including the large feature (Fig. 3C). Only the marks P_1 (a result of the first activation pulses) and P_2 (a result of the second series of pulses) remained. The bump at position f in the upper right area

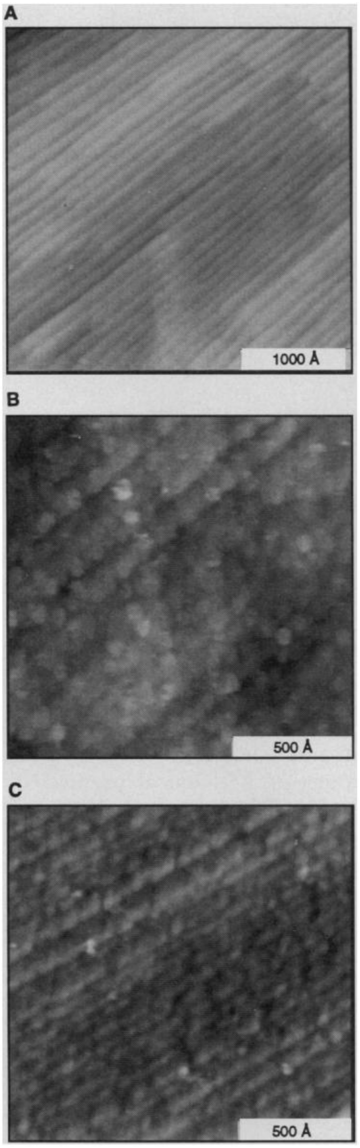

Fig. 1. Three STM images of a Pt(111) surface covered with hydrocarbon species generated by exposure to propylene gas. Images taken in constant-height mode at 0.1-V bias and 1.3 nA of current. (**A**) After adsorption at room temperature. The propylidyne ($\equiv C-CH_2-CH_3$) species that formed was too mobile on the surface to be visible. The surface looks similar to that of the clean surface. Terraces (~100 Å wide) and monatomic steps are the only visible features. (**B**) After heating the adsorbed propylidyne to 550 K, clusters form by polymerization of the C_xH_y fragments. The clusters are of approximately round shape with a diameter equal to the terrace width. They form rows covering the entire image in the direction of the step edges. (**C**) Rows of clusters formed after heating to 700 K. At this higher temperature, the carbonaceous clusters are more compact and slightly smaller in size, as they evolve to the graphitic form when H is lost completely.

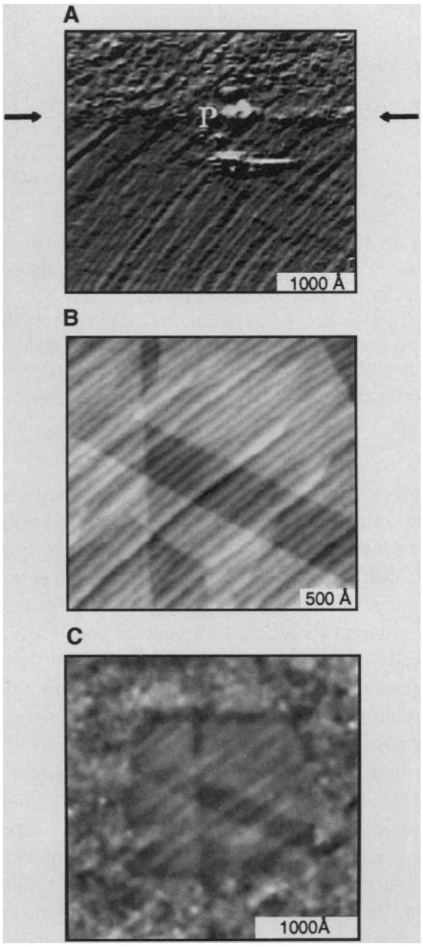

Fig. 2. The catalytic action of the STM Pt-Rh tip on a surface covered by carbonaceous clusters, as in Fig. 1B. Imaging was done in 1 atm of a mixture of propylene (10%) and H_2 (90%) at room temperature. (**A**) Carbon clusters were imaged in the top third of the image while the tip was inactive. A voltage pulse of 0.9 V was applied at the position marked P, leaving a mound of material 15 Å high. This process produced a chemically active Pt-Rh tip that catalyzed the removal of all clusters in the remaining two-thirds of the image. Only the lines corresponding to the steps are visible. This image was illuminated from a near-incident angle to enhance the transition region where the tip was switched to its active state. (**B**) While the tip was in this catalytically active state, another area was imaged, and all of the clusters were again removed. (**C**) A slightly larger image of the area shown in (B) (center square of this image), obtained after the tip was "deactivated," presumably by contamination. The active-tip lifetime was on the order of minutes.

also remained from the large feature in Fig. 3, A and B. This indicates that these residual bumps were made of chemically inactive materials that could not be rehydrogenated by the tip.

We believe that the catalytic action by the active tip, which is presumably clean Pt-Rh, consists of the atomization of H_2 from the gas phase and the hydrogenation of the C bonds of the clusters under it. Once hydrogenated, the cluster is dissolved and remains invisible to the STM. This could be a result of either desorption of the hydrogenated fragments or their rapid diffusion on the surface, like the propylidyne and ethylidyne fragments that remain invisible at room temperature to the STM (Fig. 4).

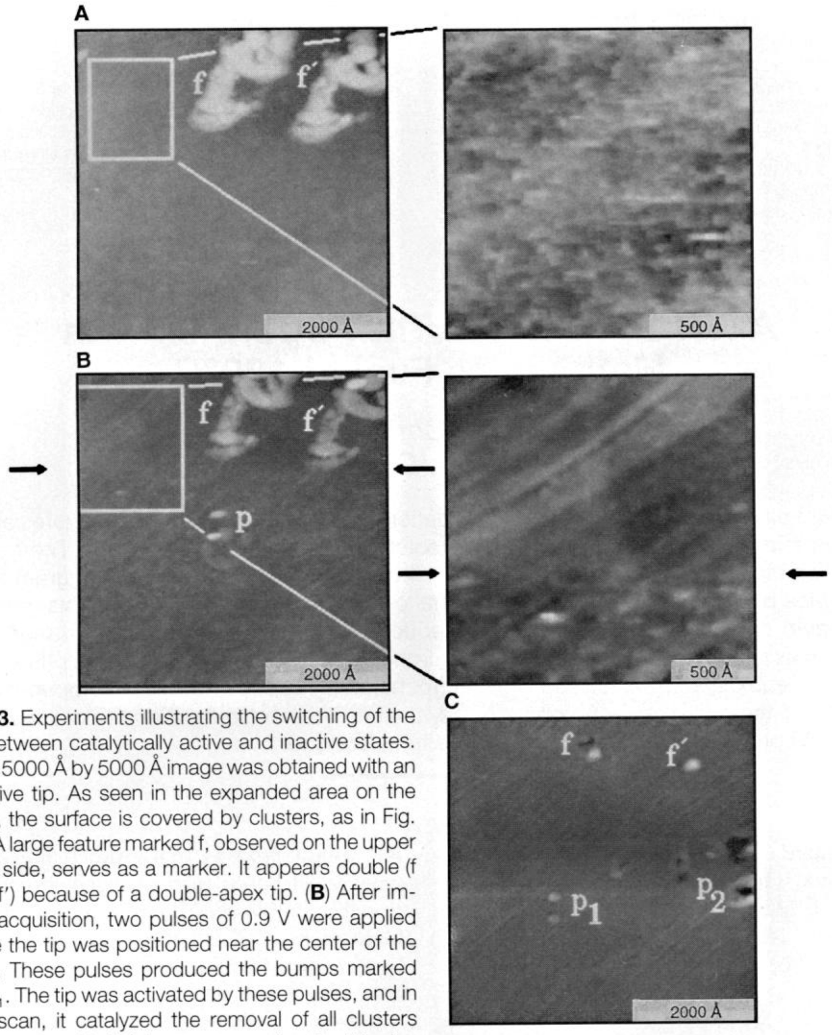

Fig. 3. Experiments illustrating the switching of the tip between catalytically active and inactive states. (**A**) A 5000 Å by 5000 Å image was obtained with an inactive tip. As seen in the expanded area on the right, the surface is covered by clusters, as in Fig. 1B. A large feature marked f, observed on the upper right side, serves as a marker. It appears double (f and f′) because of a double-apex tip. (**B**) After image acquisition, two pulses of 0.9 V were applied while the tip was positioned near the center of the area. These pulses produced the bumps marked by P_1. The tip was activated by these pulses, and in this scan, it catalyzed the removal of all clusters from the top third of the area, as well as the thinning of structure f (its height was reduced by 50% after this scan). At the line marked by the arrows, the tip suddenly became inactive, and no cluster removal occurred in the bottom two-thirds of the image. See expanded area on the right of (B). (**C**) Two additional pulses (at position marked P_2) restored once more the activity of the tip, and the subsequent scan removed all carbonaceous clusters, including the large feature f, where a bump remained that was probably made of chemically inert material.

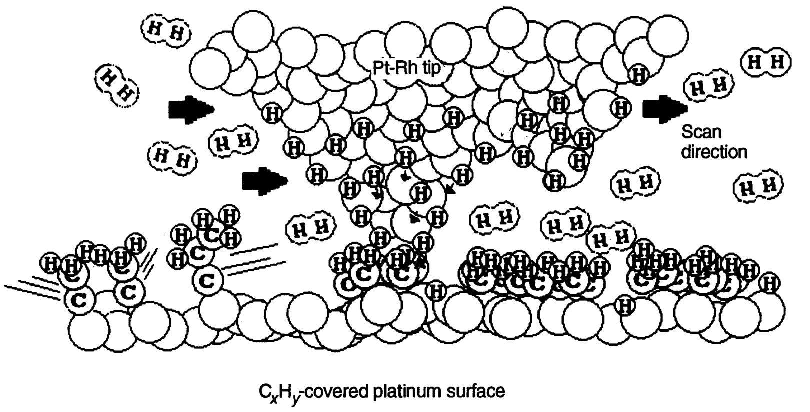

Fig. 4. The proposed model for the catalytic action by the active tip, which assumes a Pt-Rh tip with atomized hydrogen at the apex, which hydrogenates the C bonds of the clusters under it.

To further ascertain the proposed catalytic action of the STM tip, we performed numerous other experiments (8). The hydrocarbon clusters were not removed after bias pulsing in any case when the platinum STM tip was replaced with a gold tip. The tip catalysis did not appear to depend on electric field or polarity, as checked by changing the bias voltage. However, a very significant pressure dependency was observed such that the tip catalysis stopped altogether somewhere between 0.5 and 5 torr of hydrogen-propylene.

Also, tip catalysis occurred in pure hydrogen at least as efficiently as in the hydrogen-propylene mixture. In fact, the tip catalysis occurred in pure hydrogen pressures two orders of magnitude lower than the minimum pressure for the hydrogen-propylene mixture. This indicates that the propylene either did not have a significant effect or maybe even poisoned the tip catalysis by chemisorbing to the end of the STM tip and preventing hydrogen transfer.

By varying the tip-surface distance, we showed that the tip catalysis is enhanced when the tip is closer to the surface, indicating a proximity effect as would be required for the transfer of H atoms to the surface. One can dismiss the possibility of the tip mechanically removing or displacing the clusters because large areas (>5000 Å on a side) were cleaned of clusters by an active tip without visible deposits of material being observed at the edges of the empty areas. After over 1 hour, the areas remained "clean"; in other words, there was no discernible back-diffusion of the clusters. Over the course of hundreds of experiments, the buildup of material was never observed. Such accumulation following mechanical removal has been observed previously by others (9). Finally, no rehydrogenation was observed when the carbonaceous deposits were formed by decomposition above 800 K. At this temperature, the degree of dehydrogenation was very large and graphitic clusters were produced that are much more difficult to rehydrogenate.

These results clearly demonstrate the local catalytic activity of the STM tip and suggest a wealth of other experiments that can provide deep insights into the nature of the atomic-scale structure and kinetics of the catalytic action. It is still not clear by what mechanism the H is activated by the tip and transferred to the carbonaceous fragments. It is known that hydrogen readily dissociates over platinum even below 300 K, as shown by H_2-D_2 exchange studies (*10*). Because the residence time of the tip over the area occupied by one cluster is on the order of milliseconds at our scanning speeds, the turnover frequency of the H transfer reaction from the tip is about 2×10^3 s^{-1} per Pt site (assuming the atoms are being transferred from a single Pt atom on the STM tip). This is about an order of magnitude higher than that expected from comparable studies of the hydrogenation of ethylene and propylene under similar conditions (*11*) and several orders of magnitude higher than hydrogenolysis of C_xH_y species (*12*). However, these differences are not surprising because it is not necessary for these molecules to be completely hydrogenated and removed from the surface in order for them to be unobservable by the STM.

Isotope exchange reactions of hydrocarbons with deuterium gas on Pt(111) have shown that the exchange kinetics at low conversions displayed zero activation energy, a first-order dependence on D_2 pressure, and a strong negative-order dependence on the surface coverage by strongly bound carbonaceous species (*13, 14*). This negative-order dependence arises from the inhibition of dissociative chemisorption of deuterium molecules by the carbonaceous deposits. It was found that the rate of dissociative deuterium chemisorption on the platinum surfaces that are partially covered by strongly chemisorbed carbonaceous species controlled the overall exchange kinetics. From these observations, it could be argued that in our case, the STM tip acted as a source of activated hydrogen, eliminating the need for a site for dissociative hydrogen chemisorption on the surface and, as a result, significantly increased the rate of conversion of the hydrocarbon clusters.

We believe that these results demonstrating the catalytic action of the STM tip open the way for experiments that will allow the study of the local catalytic activity of surface sites and defects that can at present only be studied in an average way with the more conventional tools and methods.

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A Redox Fuel Cell That Operates with Methane as Fuel at 120°C

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Platinum black efficiently catalyzes the oxidation of methane by iron(III) to generate carbon dioxide and eight equivalents of iron(II) in solutions of sulfuric acid in water. The rate of oxidation increases over 4 hours to reach ~4.83×10^{-2} moles of iron(II) per gram atom of surface platinum per second. A redox fuel cell was assembled that used this reaction in a liquid reformer to generate soluble reducing equivalents of iron(II) from methane, which was electrochemically oxidized to iron(III) in the cell. A vanadium(V)-(IV)–nitric acid–O_2 redox system catalyzed the electrochemical reduction of O_2. The open-circuit voltage of the cell was 0.48 volt, and the maximum power output of the cell was 8.1 milliwatts per cubic centimeter of graphite felt electrode.

We have operated a redox fuel cell with methane as fuel at 120°C in which graphite felt was used as the anode and cathode. Methane is presently the most abundant hydrocarbon fuel available (*1*). Because fuel cells are capable, in theory, of converting the free energy of oxidation of a fuel directly into electrical work without the thermodynamic limitations of a heat engine (*2*), the use of fuel cells to combust CH_4 is potentially an economical and efficient method of energy production. Unfortunately, the direct oxidation of alkanes in fuel cells is slow. The use of alkanes as fuels now requires that they first be steam-reformed to generate mixtures of H_2 and CO_2 so that H_2 can be used as a fuel in a conventional, H_2-O_2 fuel cell (*2*).

König, in a 1982 German patent, reported that Pt on graphite catalyzes the oxidation of CH_4 by $Fe_2(SO_4)_3$ in acidic water to generate mixtures of Fe(II), CO_2, and CH_3OH (*3*). It was difficult to prevent complete oxidation of CH_4 to CO_2, and a flow system was required to remove CH_3OH from Pt before further oxidation occurred. The König system is among the few robust systems that catalytically activates C–H bonds in the presence of functionalized molecules (H_2SO_4 in water) (*1*). Confirmation of the König report has not been reported, and rate, yield, and turnover data have not been obtained.

We have confirmed that the König system does catalytically activate C–H bonds under certain, reproducible conditions, and we have determined the rate and stoichiometry of the reaction under these conditions. Further, we circumvented the kinetic limitations of the direct electrochemical oxidation of CH_4 by using the König system as an intermediary redox catalyst that transferred electrons from CH_4 to the anode of a redox fuel cell (Fig. 1). We chose the König system because it operates under conditions similar to those in fuel cells (strong, aqueous acid) and because it effects the complete oxidation of CH_4. Although several reports have described redox catalysts in fuel cells that use H_2 (*4*), coal (*5*), and CO (*6*) as fuels, CH_4 has not been used previously to drive a redox fuel cell.

Methane was oxidized by Fe(III) with a catalytic amount of Pt black in a static reactor system [a T316 stainless steel bomb with a glass liner (*7*)] to generate CO_2 and eight equivalents (eq) of Fe(II) (Fig. 1) [1.02 mol % of Pt relative to starting

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