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Liquid-Phase Hydrogenation of Cyclohexene over Pt Foil Catalysts

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A liquid-phase reaction cell, coupled to an ultrahigh-vacuum surface analysis chamber, was built to study liquid-phase hydrogenation reactions on small area model catalyst surfaces. The hydrogenation of cyclohexene to cyclohexane was studied at about 1.5 atm total pressure of H_2 and as a function of temperature in the 313–333 K range in liquid cyclohexene. The hydrogenation rate of cyclohexene on a clean Pt surface increased with the increasing circulation velocity of the liquid, indicating that the reaction rate was controlled by hydrogen diffusion to the surface. When the surface reaction rate was reduced by the deposition of hydrocarbon fragments on the platinum surface, the rate of cyclohexene hydrogenation became independent of hydrogen diffusion and became controlled by the kinetics of the surface reaction. The estimated activation energy of the reaction is 6 kcal/mol for cyclohexene hydrogenation on a platinum foil that was partly covered with carbonaceous deposits.

1. INTRODUCTION

Liquid-phase reactions carried out at or near 300 K, like the hydrogenation of olefins or nitriles, are important to chemical technology. It is also of considerable interest to compare and correlate rates and selectivity of catalytic reactions carried out at solid–liquid vs solid–gas interfaces under otherwise identical experimental conditions. Such comparisons and correlations allow us to learn about changes of reaction mechanism with changes in the reactant phase. We designed gas-phase (1–4) and liquid-phase (5) reaction cells in combination with ultrahigh-vacuum surface analysis chambers to study catalytic reactions over low-surface-area model catalysts that were properly cleaned and characterized before and after the reaction by a combination of surface science techniques. In this article we report the hydrogenation of cyclohexene using a polycrystalline platinum foil as the catalyst. The hydrogenation of cyclohexene on the clean metal surface is so rapid that the rate is controlled by hydrogen diffusion to the surface at about 300 K. However, the rate of cyclohexane production on a partially contaminated platinum surface became surface reaction limited. The activation energies are 15 kcal/mol and 6 kcal/mol in the diffusion-controlled and surface reaction-controlled regimes, respectively.

2. EXPERIMENTAL

The apparatus and procedure we used to perform the experiments are described in detail in Ref. (5). The main characteristics of our apparatus (shown in Fig. 1) are as follows:

(a) The UHV chamber had a base pressure of 1×10^{-9} Torr, which remained constant during the liquid–phase reaction. The sample could be cleaned in the UHV chamber by argon sputtering and oxygen heat treatments.

(b) The sample was mounted at the end of two long $\frac{1}{4}$-in.-o.d. stainless-steel tubes. It could be resistively heated or cooled by circulating liquid nitrogen through the tubes.

(c) During the transfer from UHV to the liquid reaction cell, the sample was moved vertically down to the cell in two steps. First, a hydraulic system closes a cylinder around the sample, isolating it from the rest of the UHV chamber. The inside of the cylinder was then pumped by a diffusion pump, keeping the pressure in the 10^{-8} Torr range. After opening the gate valve at the bottom of the cylinder to access the cell, the sample could be lowered to its reaction position by an 8-in.-long transfer arm.

(d) To allow good mass transfer at the liquid–solid interface, a small gear pump produced a liquid jet (velocity of up to 6 m/s) which was impinged on the surface, thus creating a thin liquid film.

(e) The total pressure during the reaction could go up to 2 atm, while the temperature of the liquid could be adjusted up to 70°C.

(f) A septum on the side of the cell allowed sampling for chromatographic analysis which monitored the progress of the reaction.

The 0.1-mm-thick Pt foil (99.995% pure) of 1 cm^2 was spotwelded to the sample holder with Pt wires. Sample cleaning was achieved by cycles of Ar^+ sputtering at 900–1000 K (5×10^{-5} Torr Ar, 1.0 keV, 30 min) followed by

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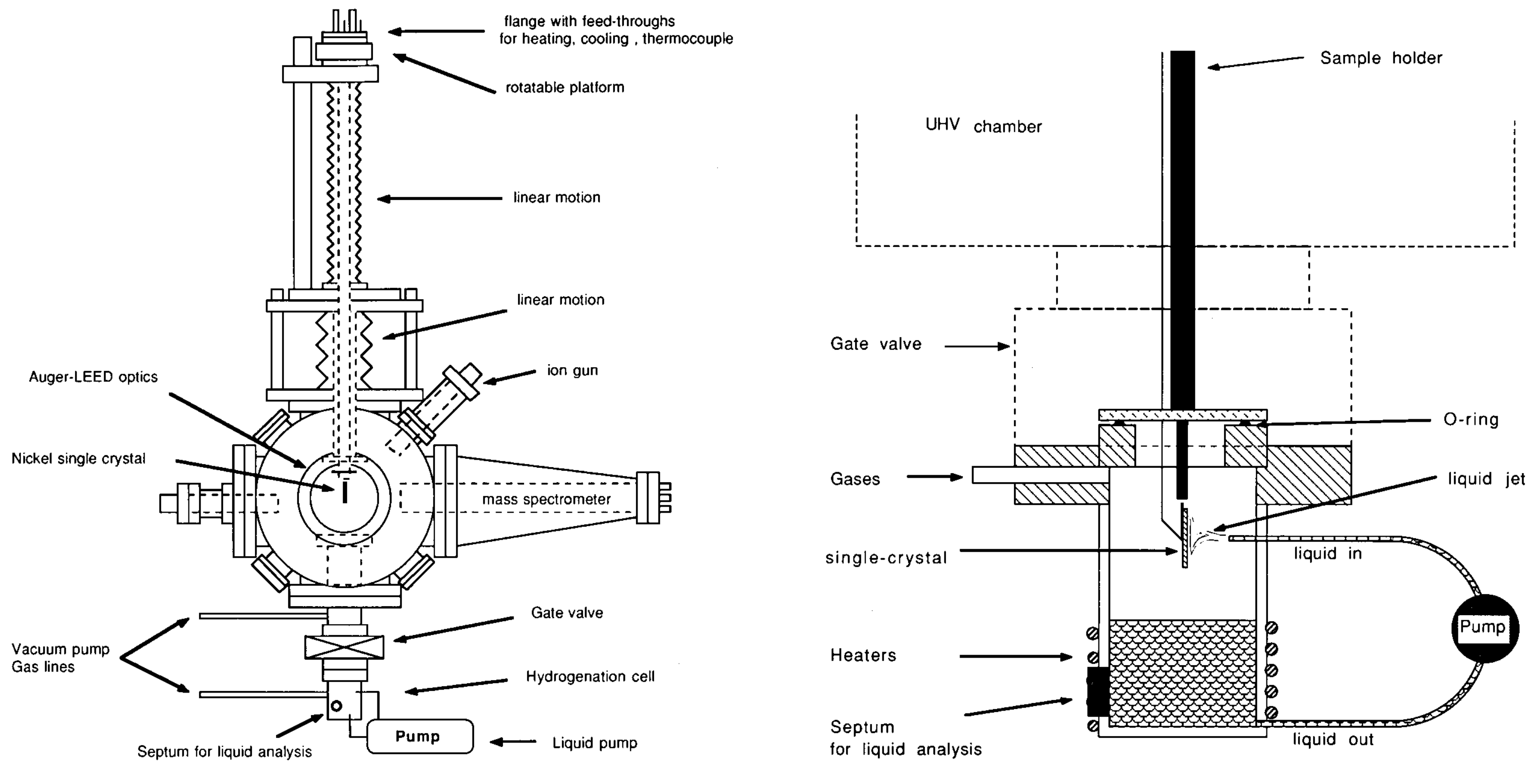

Liquid-phase hydrogenation chamber :
Surface preparation and characterisation position

Liquid phase hydrogenation cell

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FIG. 1. Liquid-phase hydrogenation chamber: Surface preparation and characterization position (left) and liquid-phase hydrogenation cell (right). The inside of the cell is gold plated to prevent background activity of the copper walls of the cell. During the reaction a liquid jet, produced by a gear pump, is impinged on the sample surface. The liquid can be heated by a heating cord tied around the cell and controlled by a temperature controller which reads the temperature at the sample surface. Hydrogen gas is introduced before the liquid hydrocarbon.

heating in 2×10^{-7} Torr O_2 at 700–800 K for 5–10 min. The cleanliness of the surface was checked by Auger electron spectroscopy. The sample was then annealed in vacuum for 5 min at 1100 K. It was necessary to wait for a few minutes for the temperature of the sample to decrease below 343 K before starting the experiment.

The reagents used are listed in Table 1. Before introduction into the reaction cell, the liquid reagents were degassed and purified in a two-compartment glass manifold that permitted freeze–pump–thaw cycles of the liquid. The transfer of the liquid into the reaction cell was made using pressurized helium (purified by circulating through a liquid nitrogen bath).

One of the main difficulties in working with cyclohexene is the presence of stable cyclohexene epoxide which forms when cyclohexene comes in contact with air. Since a 1-cm^2 surface area catalyst was used, the elimination of cyclohexene epoxide and other contaminants was of crucial importance. To achieve that goal, the 99% pure cyclohexene was treated by refluxing over CaH_2 for 2 h. The cyclohexene was then stored with excess CaH_2 under an argon atmosphere. The liquid (40 ml) was introduced into the glass manifold by a syringe. After a series of four freeze–pump–thaw cycles, the cyclohexene was evaporated into a second compartment, where it was heated up to the reaction temperature. At the same time, the 0.1-mm-thick platinum foil was cleaned by argon ion sputtering and oxygen treatment so the experiment could be performed immediately after both the catalyst and reagents were prepared. The platinum foil was transferred from vacuum into the reaction cell followed by 32.5 ml of cyclohexene pushed by helium back pressure. The hydrogen pressure in the cell was then adjusted to the desired reaction pressure. In this series of experiments, a total pressure of 1.5 atm was used. The liquid circulation pump was turned on, which produced a jet of liquid cyclohexene impinging on the sample surface. This set the starting time of the reaction. The progress of the reaction was monitored by gas chromatography (HP5790A). A 4-ft section of a $\frac{1}{8}$-in.-o.d. stainless-steel column filled with TCEQ was used to separate the cyclohexane product from the cyclohexene. Because of the very large difference between the surface area of the cyclohexane peak and the cyclohexene peak due to the large excess of cyclohexene, 2 μl of *n*-hexane and methylcyclopentane were added at the beginning of the experiment to the reactant as internal standards. In Fig. 2, we show a typical chromatogram that was obtained. During the analysis, both the ratio of cyclohexane to methylcyclopentane and the ratio of cyclohexene to *n*-hexane were measured. A calibration of our analysis was made by adding a determined quantity of cyclohexane (weighed with a precision of 0.1 mg) to the 32.5 ml of cyclohexene.

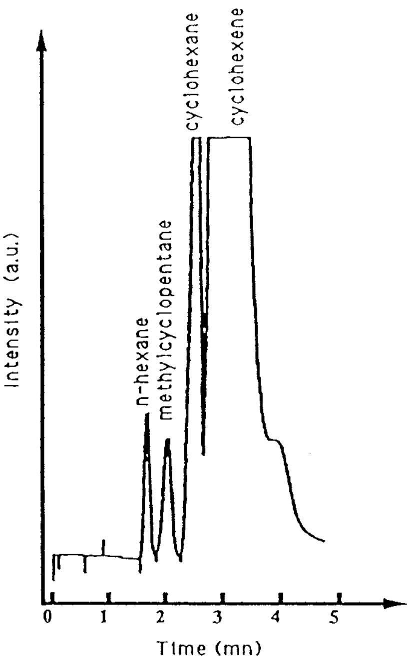

FIG. 2. A typical chromatogram during the analysis of the formation of cyclohexane in cyclohexene. Added *n*-hexane and methylcyclopentane are used as internal standards.

TABLE 1

Reagents Used for the Hydrogenation of Cyclohexene Studies

Reagent	Source	Purity (wt%)
Cyclohexene (C_6H_{10})	Aldrich	>99%
Hydrogen (H_2)	Liquid air	Liquid air
Helium (He)	Liquid air	Liquid air

3. RESULTS OF CYCLOHEXENE HYDROGENATION OVER Pt FOIL CATALYSTS

The hydrogenation of cyclohexene has been studied on various platinum catalysts both in gas phase (6) and liquid phase (7, 8). Gas-phase hydrogenation rates on model crystal surfaces [Pt(223)] have been reported in the literature over a wide range of gas pressures (9). In the following sections we report our liquid-phase data.

3.1. Reaction Rate at 323 K

The reaction rate studies were initiated in two different sequences, each yielding different results: (1) Hydrogen was introduced in the reaction cell first followed by the olefin, cyclohexene, and (2) cyclohexene was added first followed by hydrogen. When hydrogen was introduced first the platinum foil catalyst remained clean during the reaction as shown *ex situ* by Auger electron spectroscopy (AES). AES could be taken after the sample was returned to the UHV chamber. When the olefin was introduced first, carbonaceous fragments formed as indicated by the postreaction Auger spectra. Thus, in these circumstances, the reaction proceeded on a partially carbon-contaminated platinum surface. The level of Pt surface contamination depended on the time delay between introducing the olefin and the hydrogen.

In Fig. 3 the rate of formation of cyclohexane is plotted as a function of jet velocity for a clean platinum foil and a partially carbon-contaminated model catalyst. On clean platinum the rate increases continuously with jet velocity. As long as the rate of reaction increases with jet velocity the reaction is H_2 diffusion limited. Apparently the surface reaction rate is always faster than the rate of H_2 diffusion to the platinum surface in our temperature and pressure range. When olefin was introduced first, a different reaction behavior was observed as the jet velocity was increased. The rates are slower as compared to those when H_2 was introduced first. Above 5 m/s the rate of reaction reached a constant value, independent of jet velocity. In this circumstance the rate became slower and was reaction limited. Obviously, introducing olefin first caused partial decomposition of the olefin on the Pt foil and hydrocarbon fragments contaminated the surface and caused a substantial reduction in reaction rate. This permitted us to reach conditions under which the rate was surface reaction limited. This behavior demonstrates the crossover from the mass transfer-limited regime to the surface kinetics-controlled regime. In the low-jet-velocity regime, the rate of cyclohexane formation was limited by hydrogen diffusion to the boundary layer at the liquid–solid interface. The rate measured in this circumstance depended on the flux of hydrogen diffusion from the liquid to the platinum surface. At higher jet velocities, the rate measured was no longer diffusion limited and therefore was due to the kinetics of the surface reaction. Under steady-state reaction conditions (at a liquid jet velocity higher than 5 m/s) we estimate the effective liquid film thickness on the platinum foil to be about 10 μm, the hydrogen contact time to be between 0.1 and 1.0 s, and the hydrogen diffusion coefficient to be $\sim 10^{-5}$ cm^2/s. We believe the concentration of hydrogen in cyclohexene has reached phase equilibrium under our reaction conditions.

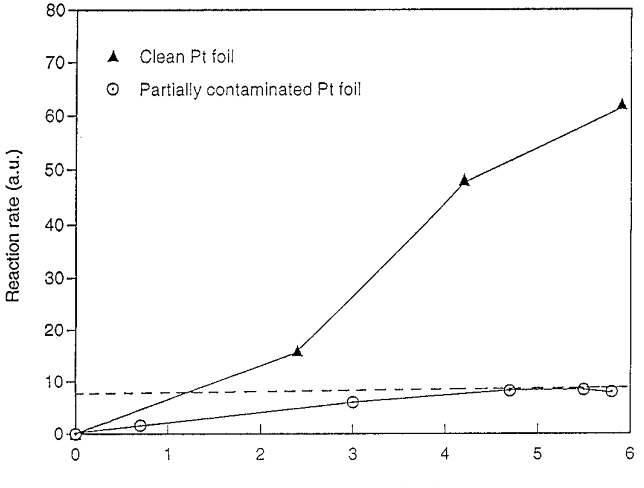

FIG. 3. Cyclohexene hydrogenation reaction rate vs liquid jet velocity at $T = 323$ K and $P = 1.5$ atm. The reaction on the clean platinum foil could not overcome the diffusion limitation because of the very fast reaction rate (▲). While on the partially contaminated platinum foil (⊙), in the low-jet-velocity regime, the rate of cyclohexane formation was limited by hydrogen diffusion in the boundary layer at the liquid–solid interface. The rate measured in this circumstance corresponded to the flux of hydrogen from the liquid to the platinum surface. At higher jet velocities, the rate measured was no longer diffusion limited and, therefore, was a measurement of the pure reaction kinetics.

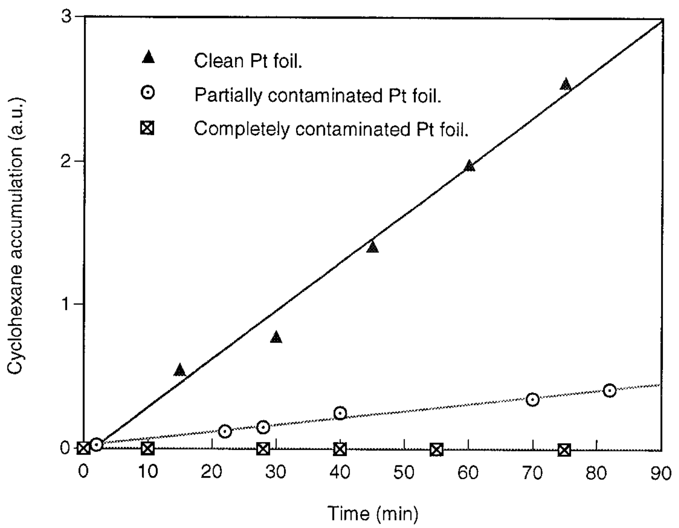

FIG. 4. Cyclohexane accumulation curve during the reaction of 32.5 ml of cyclohexene on a 1-cm^2 clean platinum foil (▲), on a partially contaminated platinum foil (⊙), and on a hydrocarbon-contaminated platinum foil (⊠) at $T = 323$ K, $P = 1.5$ atm.

The cyclohexene accumulation curve on both a partially contaminated Pt foil surface and a clean Pt foil surface for a reaction temperature of 323 K and a jet velocity of 5.8 m/s are shown in Fig. 4. A blank experiment, shown on the same graph, was performed by carrying out the reaction on a completely hydrocarbon-contaminated platinum foil. The total conversion of cyclohexene to cyclohexane after a reaction time of 80 min was 2.8×10^{-3} mol% when the liquid was introduced first, while the total conversion was 2.0×10^{-2} mol% after a reaction time of 80 min on a clean Pt surface under the same reaction conditions. The calculated turnover rates for these conditions, assuming that 10^{15} surface platinum atoms are active, were 1.1 molecules of cyclohexene/site/s in the contaminated case and 7.5 molecules/site/s in the clean case. The rate on the clean surface was almost the same as that reported by Madon *et al.* (7) for liquid-phase hydrogenation on a supported platinum catalyst.

These results illustrate the importance of having a high enough liquid jet velocity at the sample surface to measure the kinetics of liquid-phase catalytic reactions and to avoid mass transfer limitations due to the diffusion of reactants or products in the liquid phase. Alternatively, this can be achieved by slowing down the surface reaction rate by partial contamination of the active catalyst surface.

After the reaction, when the platinum foil was transferred back to UHV, Auger spectra showed the surface to be covered by a large amount of carbon species. Some of these hydrocarbon species were strongly chemisorbed cyclohexene, which could be desorbed intact from the surface by heating the sample.

3.2. Reaction Rate as a Function of Temperature

The rate of hydrogenation of cyclohexene was measured at various temperatures between 313 and 333 K, under the same conditions as those described for 323 K. In Fig. 5, the results are shown in an Arrhenius plot. The activation energy for the hydrogenation of cyclohexene to cyclohexane on a polycrystalline Pt foil was estimated to be 6 kcal/mol when the surface reaction is rate limiting (partially carbon-contaminated catalyst), which is close to the activation energy estimated by Madon *et al.* for a supported Pt catalyst (7). It should be noted that work conducted on a contaminated surface did not appear to affect the activation energy of this reaction compared with literature values (7). The apparent activation energy for the diffusion-controlled reaction in the presence of the clean Pt foil was about 15 kcal/mol.

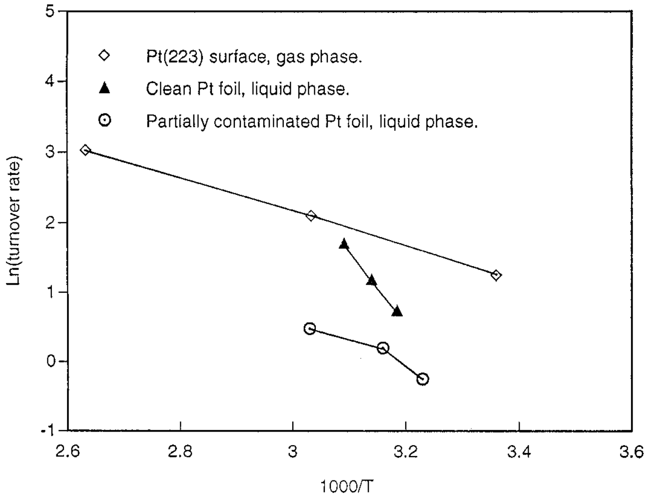

FIG. 5. Arrhenius plot of ln(rate) vs 1000/T for cyclohexene hydrogenation over Pt(223) crystal face at a total pressure of 77 Torr in the gas phase (9) (◇), over a clean Pt foil in the liquid phase (▲), and over a partially contaminated Pt foil in the liquid phase (⊙).

The hydrogenation rate of cyclohexene in the gas phase reported for a stepped Pt(223) single-crystal surface was significantly faster than any of the liquid hydrogenation rates reported above (9). Larger gas-phase rates were also reported by Madon *et al.* using high-surface-area silica-supported platinum catalysts. To the best of our knowledge, this is the first reaction for which kinetic data are available under similar conditions for both gas- and liquid-phase reactions. Therefore, the question arises as to the origin of the rate differences. First, it should be noted that for the clean samples our results were always in the diffusion-controlled limit. Therefore, it cannot be determined with certainty whether faster liquid jet velocities would have allowed liquid-phase hydrogenation rates to approach those of the gas phase. However, we see no fundamental reason why gas-phase rates should not ultimately be obtainable for this particular reaction under the reaction conditions that were employed. The reactant concentration is in large excess (low conversion) and the product (cyclohexane) has much lower sticking probability than the reactant (cyclohexene). Gas-phase olefin hydrogenation reactions are often zero order in their hydrocarbon component, just as in the liquid phase, and the major variable determining the reaction rate is the delivery of hydrogen to the catalyst surface. Provided that fast enough jet velocities were available, the liquid- and gas-phase rates could indeed be the same in the absence of surface contamination by impurities. In other circumstances reaction rates in the liquid phase are likely to be appreciably lower than in the gas phase for diverse reasons. The product is more sticky than the reactant for some reactions and may cause product poisoning even at low conversion. In some cases an inert solvent, such as water or alcohol, that could compete with the reactant molecules for adsorption sites may be used. For the hydrogenation of cyclohexene, however, solvent effects were negligible as reported by Madon *et al.* (7). Of course impurities are more likely to influence the results of liquid-phase studies than those for experiments in the gas phase because of the ease of liquid contamination relative to that of the vapor.

The rate of hydrogenation was observed to be heavily dependent on the cleanliness of the sample and the order in which the reactants were introduced into the hydrogenation cell. This phenomenon has often been observed for single-crystal studies (10). It seems in general that single crystals do the same catalysis as their supported counterparts, but that they poison much more easily. It is likely that the support plays an important role in keeping the catalyst clean. In the case of metal crystals and foils, however, introduction of hydrocarbons in the absence of hydrogen cause the formation of hydrocarbon decomposition products which most likely lead to the deceleration of the reaction rate. This was indeed fortunate in the present case, because it permitted the reaction to be carried out in the surface kinetic-limited regime instead of being hydrogen diffusion controlled.

4. CONCLUSION

The liquid-phase reaction cell/UHV apparatus developed in our laboratory was used to study liquid-phase catalytic reactions on well-characterized surfaces. We have been able to carry out the hydrogenation of cyclohexene on a clean Pt foil of 1-cm^2 surface area. The diffusion of hydrogen to the liquid–solid interface controlled the reaction rate over a clean Pt surface. When using a partially carbon-contaminated Pt surface that decelerated the surface reaction rate we could overcome mass transfer limitation at a liquid jet velocity higher than 5 m/s. We were able to vary the reaction temperature from 313 to 333 K. The estimated activation energy is 6 kcal/mol for the surface kinetics-controlled reaction, which is comparable to literature values for this reaction on supported Pt catalysts (7). An apparent activation energy of 15 kcal/mol was obtained for the reaction in the diffusion controlled regime on the clean Pt surface. Hydrogen seems to protect the surface from hydrocarbon contamination during the solid–liquid interface reaction.

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