Fraction of Pt Surface Covered with Coke Following Hydrogenolysis of Hexane

F. J. Rivera-Latas, R. A. Dalla Betta, and M. Boudart
Dept. of Chemical Engineering, Stanford University, Stanford, CA 94305

Following hydrogenolysis of n-hexane on an alumina-supported platinum catalyst, the surface of the metal is covered partially with carbonaceous residues or coke. The fraction of surface platinum not covered with coke has been found to be about one half by four independent techniques: titration of preadsorbed oxygen by dihydrogen, chemisorption of carbon monoxide, infrared spectroscopy of chemisorbed carbon monoxide, and hydrogenation rate of ethylene. The first of these techniques suggests itself as the simplest one for further studies of deactivation by coking of platinum catalysts.

Objectives, Relevance and Significant Prior Work

Catalytic naphtha reforming plays a major role in satisfying the demand for unleaded high-octane gasoline. In this process, the reactants are C_5 to C_{10} hydrocarbons and dihydrogen. They react in the presence of a bifunctional catalyst around 770 K between 10 and 35 bar. The catalyst is bifunctional with both metallic and acidic components. The metallic phase consists of Pt clusters or bimetallic clusters of Pt and another metal. The acidic component is on the support, that is, alumina acidified with chlorine. The metallic phase is responsible for dehydrogenation and dehydrocyclization, while the acidic component catalyzes isomerization and hydrogenolysis. In practice, the catalyst is pretreated in sulfur-containing feed to moderate the activity of the metal phase for hydrogenolysis. A chlorine compound and traces of water are introduced with the reactant mixture to keep a constant content of chlorine on the support (Sinfelt, 1981; Gates et al., 1979).

During operation, hydrogen-containing carbonaceous deposits are formed on the surface of the catalyst. These deposits, called *coke*, decrease the rate of reforming (Marin and Froment, 1982; Franck and Martino, 1985). This deactivation must be controlled to improve the economics of reforming (Sinfelt, 1981). The nature of coke and its deactivation effect depend on the reaction, the catalyst, and the process conditions. Most of the literature about the subject deals with processes other than catalytic reforming (Butt, 1984; Wolf and Alfani, 1982). Here we deal only with coking in catalytic naphtha reforming, a subject that has recently been reviewed (Biswas et al., 1988).

The rate of coke deposition on a Pt/Al_2O_3 catalyst is very high at the beginning of reforming (Sinfelt, 1981; Gates et al., 1979; Marin and Froment, 1982; Franck and Martino, 1985) and then slows down because of deactivation of the active centers responsible for the formation of coke precursors and of coke from the precursors. These precursors are believed to be unsaturated species formed mainly on the platinum surface. Some form coke on the metal and some migrate to the alumina support where they also end up as coke, as shown by Myers et al. (1961) and Parera et al. (1983). Increasing the platinum content of the catalyst increases the formation of coke (Beltramini et al., 1985). The precursors polymerize to polycyclic compounds either on the platinum or on the support (Myers et al., 1961). Hence, the platinum surface is expected to become partially covered with coke. The question asked in this article is: what is the fraction of the platinum surface covered with coke following a typical reforming reaction?

Interest in this question was recently raised by Davis et al. (1982), who studied strongly adsorbed hydrocarbon deposits on platinum single crystals following several hydrocarbon-dihydrogen reactions at atmospheric pressure between 300 K and 700 K. From carbon-monoxide adsorption-desorption studies, Davis et al. concluded that 75% to 98% of the platinum surface was covered by carbonaceous species, the extent of coverage and the structure of the carbonaceous layer depending on temperature. After reaction at higher temperature, the coverage was higher and the carbon layer became three dimensional.

To assess the relevance to naphtha reforming of these observations on single crystals of platinum, we prepared a platinum-alumina (Pt/Al_2O_3) catalyst with a high metal content

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Correspondence concerning this article should be addressed to M. Boudart.

(5 wt. %) to enhance the sensitivity of experiments designed to examine the platinum surface following *n*-hexane hydrogenolysis at atmospheric pressure and 713 K. This reaction was selected because it is a good model reaction for catalytic reforming (Franck and Martino, 1985), and it was also studied by Davis et al. (1982), in the higher temperature range of their work on platinum single crystals.

Following hexane hydrogenolysis, the fraction of surface platinum atoms exposed was measured by four independent techniques: titration of pre-adsorbed oxygen by dihydrogen, chemisorption of carbon monoxide, infrared spectroscopy of carbon monoxide bonded to platinum, and rate of ethylene hydrogenation. Indeed, the chosen selective gas chemisorption techniques measure directly the number of metal atoms exposed on supported metal samples (Boudart and Djéga-Mariadassou, 1984). Besides, ethylene hydrogenation is a good kinetic probe to measure the fraction of platinum atoms exposed. Indeed, the reaction is a structure-insensitive reaction whose turnover rate, that is, the number of molecules reacting per platinum atom and per second, is independent of surface structure (Boudart, 1977). It is similar to the hydrogenation of cyclohexene. The turnover rate for the latter reaction on platinum does not depend on the amount of sulfur-poisoning surface platinum atoms (Leclercq and Boudart, 1981).

Major Results and Conclusions

The free platinum atoms following coking was counted in almost equal number by titration of pre-adsorbed O by H_2, chemisorption of CO, IR absorption of chemisorbed CO, and hydrogenation of ethylene. The most significant result of this work is that each method indicates that approximately 50% of the platinum surface remains exposed following hexane hydrogenolysis under our conditions. Since the four methods are independent, this result appears secure. It is suggested that, in future work on the coking of platinum, the fraction of surface Pt covered with coke be determined by the simplest of the four independent methods used in our study, namely the O-H_2 titration.

The simplest explanation of the discrepancy between the 50% of surface carbon found by us and the 75% to 98% reported by the Somorjai group (Davis et al., 1982) on a single crystal of platinum is the mechanism proposed by the Parera group (Parera et al., 1983; Beltramini et al., 1985). It is based on the possibility of spillover of precursors of polymeric carbon from the platinum surface to the support. As a result of spillover of surface species between metal and support, a well known phenomenon in catalysis, coke precursors formed on the platinum surface migrate to the carrier by spillover and surface diffusion in the case of supported platinum. By contrast, they are removed only by desorption following partial hydrogenation in the case of platinum single crystals. Then, the concentration, residence time, and polymerization rate of these species on the platinum surface might be much larger in the case of single crystals work than on supported platinum. By contrast, these species will polymerize preferentially on the carrier surface in the case of supported platinum.

If this explanation is correct, we conclude that the results obtained with a *model* system (the single crystal of platinum) need to be corrected for the effect of the support present in the *industrial* system. Many of the results from the model system remain relevant to the industrial system. But when it comes to deactivation of the metal, the effect of spillover to the support of the commercial catalysts must be taken into account. These effects have been summarized by Parera recently (1988).

Selective Chemisorption on Coked Platinum Surfaces

Titration of pre-adsorbed oxygen by dihydrogen

Adsorbed oxygen titration by dihydrogen was used to measure the hydrogen uptake on the clean and coked catalyst as proposed by Benson and Boudart (1965). The advantage of this method is that it measures the hydrogen uptake on platinum without the necessity of previously outgassing the catalyst at high temperature until complete removal of adsorbed hydrogen. This feature makes the method well adapted to the coked catalyst, since any high-temperature treatment of the catalyst following hydrogenolysis of hexane might alter the properties and structure of the carbonaceous layer. Indeed, Davis et al. (1982) have shown that during temperature-programmed desorption (TPD) experiments, carbonaceous species release large amounts of dihydrogen from room temperature (RT) to 373 K. The method is based on the RT reaction of dihydrogen with pre-adsorbed oxygen on platinum surface atoms Pt_s which is believed to follow the stoichiometry:

$$Pt_sO + 3/2\ H_2 = Pt_sH + H_2O \qquad (1)$$

(Benson and Boudart, 1965). This stoichiometry has been discussed many times, but recent work supports it (O'Rear et al., 1990).

Irreversible chemisorption of carbon monoxide

This is a reliable and standard method for determining the surface area of supported metal catalysts (Moss, 1972). For platinum, a value of about 0.75 CO molecule per surface platinum atom counted by hydrogen chemisorption was reported for high values of the percentage of metal exposed (Benson and Boudart, 1965). Carbon monoxide displaces adsorbed H atoms on platinum at RT. The reaction stoichiometry is:

$$2\ Pt_sH + 2\ CO = 2\ Pt_sCO + H_2, \qquad (2)$$

as will be shown in this work. Thus, the method can be used to measure the fraction of surface Pt atoms exposed on the coked catalyst without outgassing it at high temperature. The results obtained by this method can be compared directly with the ones obtained by infrared spectroscopy of adsorbed CO.

Fourier transform infrared spectroscopy of adsorbed carbon monoxide

Infrared spectroscopy (FTIR) of adsorbed carbon monoxide offers a direct way to measure the fraction of exposed platinum atoms. In principle, the integrated absorption intensity A_M of an infrared vibrational band is given by the formula:

$$A_M = B \times (\delta\mu)/(\delta Q)^2$$

(Little, 1966) where B is a constant, μ is the dipole moment, and Q the normal coordinate associated with the vibrational mode. If μ and Q are coverage-independent, the integrated band intensity should increase linearly with coverage:

$$\log_e(I_o/I)dv = c \times \iota \times A_M.$$

where I_o and I are the incident and transmitted light intensities at a particular frequency v, c is the concentration of adsorbing substance, and ι is the path length through the sample. The integration is extended over the complete absorption band.

If the light absorbing molecules are strongly coupled, however, the above expression for A_M is no longer valid, and the integrated band intensity does not follow a simple linear relationship with coverage. Thus, the integrated intensity of an absorption band cannot generally be used as a measure of coverage. Deviations from linearity have been reported in the literature for the case of adsorbed carbon monoxide on Pt (Shigeishi and King, 1976; Eischens and Pliskin, 1958) and Pd (Ortega et al., 1972). This effect is not well understood, imposes a limitation in the use of infrared spectroscopy to measure CO coverage (Ortega et al., 1972), and occurs at high coverage of CO. The effect is due to strong coupling interactions between chemisorbed CO molecules (Eischens and Pliskin, 1958).

To circumvent these difficulties, infrared spectra of adsorbed CO on Pt have been measured at increasing coverage in the presence of a residual pressure of H_2. The effect of adsorbed H atoms is that of reducing the intermolecular interaction between adsorbed CO molecules. As a result, the CO integrated absorption intensity follows a linear relation with CO coverage. These observations are critically examined in the discussion section, where it is concluded that the described procedure permits measuring the fraction of surface platinum atoms exposed on both the clean and coked catalyst.

Experimental Studies

Catalyst preparation

Dihydrogen hexachloroplatinate (IV) (40% Pt, Alfa Products) was used as precursor because its high solubility permits a high loading of metal (5%) in one impregnation step. The precursor solution was prepared with double distilled and deionized water. The support was obtained by treating high-purity boehmite alumina (Catapal, Conoco) in flowing dioxygen at 776 K for 3.5 h. The pore volume of the γ-alumina is 0.52 $cm^3 \cdot g^{-1}$ as measured with water, and its composition is: 0.007% Fe_2O_3, 0.01% SiO_2, 0.005% Na_2O_3, and less than 0.013% S. The sulfur content corresponds to 1.6% of the number of platinum atoms. Dioxygen (99.9% Liquid Carbonic) was further purified through a dehydrated 3A molecular sieve at Dry-Ice acetone temperature. Dihydrogen (99.99%, Liquid Carbonic) used in these experiments and in all others reported below was further purified by diffusion through a heated palladium cell.

A batch (10 g) of 5% Pt-Al_2O_3 catalyst was prepared by incipient wetness impregnation of γ-alumina with a water solution of dihydrogen hexachloroplatinate (IV), followed by the usual treatment of drying, calcination and reduction. Drying was done in a vacuum oven at 353 K for 10 h. Then the sample was treated in O_2 flowing at a rate of 6.9 $\mu mol \cdot g^{-1} \cdot s^{-1}$, while the temperature was increased up to 673 K over 3 h. The temperature was left at 673 K for 2 h. Following evacuation at RT, the sample was reduced in H_2 flowing at a rate of 4.1 $\mu mol \cdot g^{-1} \cdot s^{-1}$, while the temperature was increased to 725 K over 5 h and left at this temperature for 2 h. The sample was evacuated at 620 K for 1.5 h, cooled down to RT, and exposed to O_2. The temperatures of treatment by O_2 (673 K) and H_2 (725 K) produce a highly dispersed (Bournonville et al., 1983) and well reduced (Foger, 1984) platinum phase. Higher reduction temperatures (≥ 770 K) were avoided since they might cause contamination of the Pt surface by species from the support (Leclercq and Boudart, 1981; Den Otter and Dautzenberg, 1978; Kunimori et al., 1983). The finished catalyst, denoted as *clean*, as opposed to *coked*, was stored in a closed flask.

Analysis of the catalyst showed a 5.15 wt. % platinum and 0.90 wt.% chlorine after drying at 420 K for 1 h. This catalyst was used in all the experiments described below. Before any experiment, the catalyst was always outgassed at 373 K for 0.5 h and treated *in situ* in dioxygen at 575 (± 5) K and 50–100 kPa for 0.2 (± 0.05) h to remove any adsorbed hydrocarbon (Schlatter and Boudart, 1972). The catalyst was treated in dihydrogen that flowed at 726 (± 2) K for 0.5 h, because it has been reported by Otero-Schipper et al. (1977) that high-temperature reduction (570–770 K) is required for attaining reproducible rates of reaction on an aged platinum catalyst. Following this treatment, the platinum surface was considered *clean*.

Hexane hydrogenolysis

Hexane hydrogenolysis deposits large amounts of carbonaceous species on supported and unsupported Pt catalysts (Marin and Froment, 1982; Davis et al., 1982). A standard Pyrex flow system was used (Rivera-Latas, 1986). A small amount of catalyst (0.02–0.2 g) was treated in dihydrogen flowing at a rate of 1.02 (± 0.02) $mmol \cdot g^{-1} \cdot s^{-1}$ at 726 (± 2) K and atmospheric pressure for 0.5 h. Then the reactor temperature was decreased to 693 (± 2) K, and dihydrogen was flowed through a bubbler containing *n*-hexane at RT and through a condenser at 288 (± 0.5) K. The reaction temperature was increased at a rate of 7.5 K/s up to 713 (± 2) K and kept at this temperature for 3 h. The reactant mixture had a dihydrogen-hydrocarbon rate of 7 (± 1), and the hexane conversion was 0.08 (± 0.03) after 1 h of reaction as measured by gas chromatography. After 3 h, the reaction was quenched by removing the oven while keeping the reactant mixture flowing. Pure H_2 was passed at RT through the reactor until no hydrocarbon remained in the gas phase. *This is the critical part of the treatment.* The coverage of the platinum surface by carbonaceous species and the chemical composition of these species may be altered by the way the reaction is stopped, in vacuum, in dihydrogen, or in the reactant mixture. The last was considered pertinent because dihydrogen pressure and the ratio of dihydrogen/hydrocarbon partial pressure affect both hydrocarbon coverage (Mahaffy and Hansen, 1979) and coke composition (Parera et al., 1983; Davis et al., 1982). Products of the reaction were analyzed in a gas chromatograph (HP 5980) with a flame ionization detector coupled with an integrator (HP 3600). A 2.5-m-long, 3-nm Chromosorb 102 column was used. The flame detector was calibrated by using a gas mixture of 1.07% methane in helium. The fraction of surface platinum atoms uncovered with carbonaceous species was measured *in situ* (that is, the catalyst was not exposed to air) by the techniques described next.

The *n*-hexane (Photrex for UV spectroscopy, Baker), following treatment (Gordon and Ford, 1972) to remove olefins and sulfur compounds, was 99.99% pure as detected by gas chromatography. Helium (99.995%, Liquid Carbonic), which was passed through both MnO/SiO_2 at RT and 5A molecular sieve at liquid dinitrogen temperature, was used to purge the system before starting the experiment.

The total conversion of hexane during hexane hydrogenolysis is reported elsewhere (Rivera-Latas, 1986). It was calculated from the product distribution data measured by gas chromatography. It decreased with time during the reaction from ≥ 0.14 at the beginning of the treatment down to 0.08 (± 0.03) after 0.5-1 h. Subsequently, the conversion did not change substantially. Deactivation is due to the formation of carbonaceous deposits on the catalyst surface. Independent gravimetric experiments (Rivera-Latas, 1986) showed that the formation rate of carbonaceous deposits decreases with time on stream reaching a quasi-constant value after 1 h of reaction. After 3 h of reaction, the carbon content of the catalyst is larger than 1 wt. %. Temperature-programmed reduction in H2 of the catalyst following hydrogenolysis yielded methane as the only product starting at 650 K with a peak maximum at 865 K (Rivera-Latas, 1986).

Chemisorption measurements

Typical adsorption isotherms of H_2 and CO were measured at RT by means of a volumetric adsorption system equipped with a Texas Instrument differential pressure gauge (Hanson, 1975). In addition, CO uptake was measured by means of an IBM (IR/98) FTIR spectrometer. Both O_2 (99.995%, Matheson U.H.P.) and CO (99.9%, Matheson) were used in these experiments. A small amount (0.2 g) of clean catalyst was outgassed under 3×10^{-3} Pa at 673 K for 1.25 (± 0.25) h and exposed to 50-100 kPa of O_2 at RT for 1 h. Following this treatment, a H_2 adsorption isotherm was measured between 5 and 30 kPa. The catalyst was evacuated under 5×10^{-3} Pa at RT, and a H_2 backsorption isotherm was measured.

A small amount (0.2 g) of coked catalyst was outgassed under 5×10^{-3} Pa at RT until constant pressure was measured. First, N_2 (99.9%, Liquid Carbonic) was introduced in the cell at 75 kPa, and then O_2 was diffused into the cell at RT. The catalyst was outgassed under 4×10^{-3} Pa and exposed again to O_2 at 50 kPa for 1 h. After evacuation at 3 mPa at RT, a H_2 adsorption isotherm was measured as before; in this case, a trap at Dry-Ice acetone temperature was used to collect any water from the gas phase. A backsorption isotherm was then measured. Adsorption isotherms of CO on the clean sample were measured to show that CO displaces H adsorbed on Pt at RT, Figure 1. The adsorption isotherms of CO were measured on a small amount of sample (0.2 g) at RT either after evacuating the sample at 675 K for 1.25 (± 0.25) h following reduction or in the presence of a residual pressure of H_2 ($<$ kPa). In both cases, the isotherms were measured between 5 and 30 kPa and with CO doses below one monolayer coverage up to 30 kPa as well. Backsorption isotherms were measured after evacuation under 3×10^{-3} Pa for 0.25 h at RT. Adsorption isotherms of CO were also measured on the coked sample after evacuation *in situ* under 5 mPa at RT. Then a CO adsorption isotherm was obtained. A backsorption isotherm was measured in the usual way.

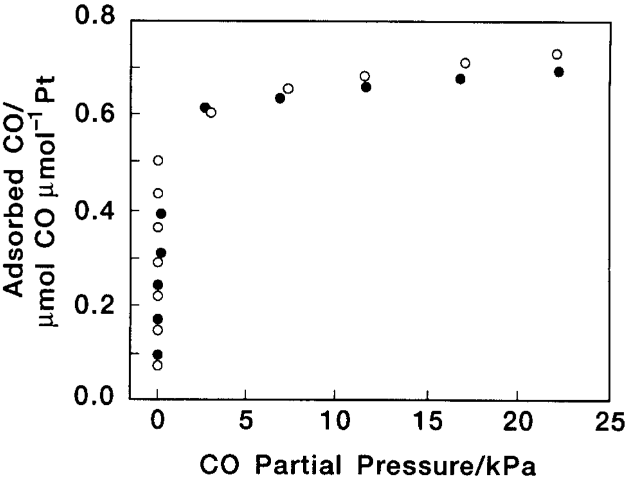

Figure 1. Carbon monoxide adsorption isotherms.
◇, measured; ◆, calculated.

The fraction of Pt atoms exposed on both the clean and coked catalysts was measured by FTIR transmission spectroscopy of carbon monoxide chemisorbed on Pt at RT.

A catalyst wafer was prepared by pressing 1.8-2.8 mg of sample under 7×1.0^4 kPa in a die of 1.27 cm diameter. The wafer was treated *in situ*, either during reduction or during hexane hydrogenolysis, in a standard infrared cell (Rivera-Latas, 1986). The cell was outgassed down to a residual pressure of H_2 of 0.3-1 kPa at RT. By inverting the cell, a transmission infrared spectrum was taken without exposing the sample to air. This spectrum was used as background in successive spectra with increasing CO coverage. Without moving the cell to avoid any artifact from changes in the background scattering, spectra were measured as successive incremental amounts of dosed CO were added. These amounts correspond to coverage between 0.008 and 10 monolayers as calculated from the O-H_2 titration. The cell was then evacuated, and another spectrum was taken. The resolution was 2-4 cm^{-1}.

Results

All the chemisorption values (Tables 1 and 2) are given in μmol of adsorbed gas, that is, H or CO per μmol of total platinum. Each table corresponds to one type of experiment performed on the sample, either clean (column 1) or coked (column 2). The third column shows the ratio of the values in columns 2 and 1. These values represent the fraction of *surface* platinum atoms exposed on the coked catalyst.

The results of the titration of pre-adsorbed O by H_2 are summarized in Table 1. Hydrogen chemisorption values were calculated by extrapolating the high-pressure linear portion of

Table 1. Fraction of Pt Surface Exposed from Titration of Adsorbed O by H_2

	Chemisorption μmol H/μmol Pt		Fraction of Pt Surface Exposed
5% Pt/γ-Al_2O_3-0.9%Cl	Clean	Coked	Coked
H/Pt $Pt_sO + 3/2\ H_2 = Pt_sH + H_2O$	0.71	0.40	0.56

Table 2. Fraction of Pt Surface Exposed from Irreversible Chemisorption of CO and FTIR Spectroscopy of Adsorbed CO

	Chemisorption μmol CO/μmol Pt		Fraction of Pt Surface Exposed
5% Pt/γ-Al_2O_3-0.9% Cl	Clean	Coked	Coked
CO/Pt $Pt_s + CO = Pt_sCO$	0.51	—	—
CO/Pt $2Pt_sH + 2CO = 2Pt_sCO + H_2$	0.50	—	0.48
CO/Pt $0.83Pt_s + 0.17Pt_sH + CO = \ldots$	—	0.24	—
CO/Pt IR Absorbance	0.52	0.26	0.50

the first H_2 adsorption isotherm to zero pressure and assuming the stoichiometry of Eq. 1.

The chemisorption values from the backsorption isotherms for the clean and coked catalysts correspond to 67% and 83% of the exposed platinum surface, respectively, as calculated above.

Rows 1 and 2 of Table 2 show the irreversible chemisorption value for the clean sample either in the absence of adsorbed H (0.51 μmol CO/μmol Pt) or in the presence of a residual pressure of H_2 (0.50 μmol CO/μmol Pt). Chemisorption of CO was determined by extrapolating the high-pressure linear portion of the isotherm to zero pressure; the difference between the extrapolated total uptake and the backsorption uptake is denoted as irreversible chemisorption. Equation 2 was assumed for the stoichiometry of adsorption of CO in the presence of a residual pressure of H_2. The good agreement between the calculated chemisorption values shown in Table 2 justifies that stoichiometry. The latter is further supported by the remarkable coincidence of the isotherms shown in Figure 1, where CO uptake vs. partial pressure of CO is plotted both as measured in the absence of adsorbed hydrogen (filled points) and as calculated from the data by means of Eq. 2 (open points). In both cases, CO was dosed in amounts below one monolayer coverage. These results demonstrate that CO displaces adsorbed H at RT, although about 30% of the adsorbed H is not removed by CO.

Row 3 of Table 2 shows the amount of CO-irreversible chemisorption for the coked catalyst following evacuation at RT (0.24 μmol CO/μmol Pt):

$$0.83\ Pt_s + 0.17\ Pt_sH + CO = Pt_sCO + 0.17/2\ H_2 \qquad (3)$$

Equation 3 was assumed for the stoichiometry of adsorption since 17% of the adsorbed H at RT is irreversibly chemisorbed, as determined separately.

From FTIR spectroscopy (Table 2), about 50% of the platinum surface remains exposed following hydrogenolysis of hexane. The CO chemisorption values for the clean (0.52 μmol CO/μmol Pt) and coked (0.26 μmol CO/μmol Pt) platinum are in very good agreement with the irreversible chemisorption values calculated from the adsorption isotherm data (Table 2). Moreover, the ratio of those values (0.50), which is assumed to be the fraction of surface Pt exposed following the hydrogenolysis reaction, agrees reasonably well with the fraction calculated from hydrogen uptake data (0.56).

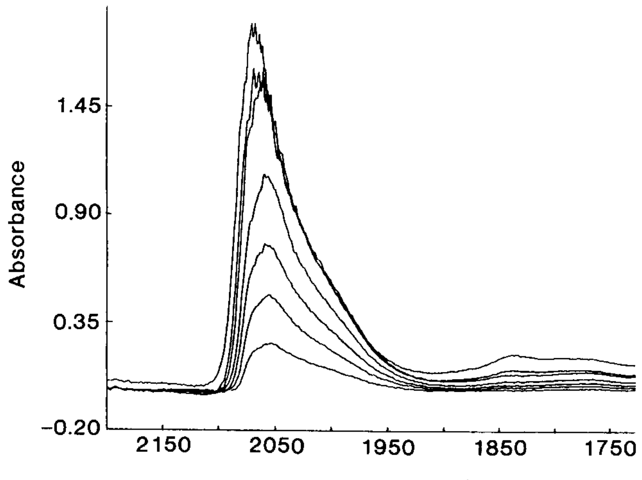

Figure 2. Infrared spectra of adsorbed carbon monoxide on clean sample with increasing coverage.

Figures 2 and 3 show the infrared absorption spectra of carbon monoxide adsorbed on platinum at increasing coverage by both the clean and coked sample, respectively. These are the spectra of the linearly bonded CO. Absorbance is plotted after subtraction of the corresponding background spectrum (the spectrum of the clean or coked sample with zero coverage of CO). A remarkable difference between clean and coked samples is that the spectrum for the clean sample shifts to higher wavenumbers and becomes more intense when the sample was evacuated at RT after full coverage in carbon monoxide was reached (Figure 4). For the coked sample, however, the spectrum does not change after evacuation. Another broad and diffuse peak appears in the range of 1,800 cm^{-1} at high coverage of CO. This is assumed to be bridge-bonded CO. This band is neglected in the analysis of the data, since its intensity is very low and about the same fraction (less than 10%) of the intensity of the band for the linearly bonded CO in each sample. Thus, this approximation should not affect significantly the value of the fraction of Pt surface exposed,

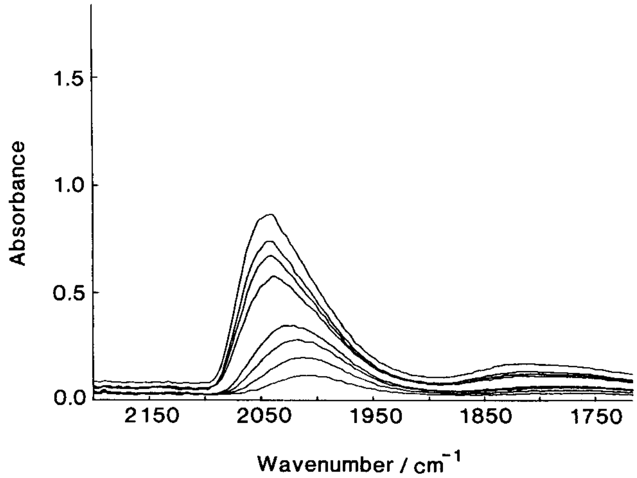

Figure 3. Infrared spectra of adsorbed CO on coked sample with increasing coverage.

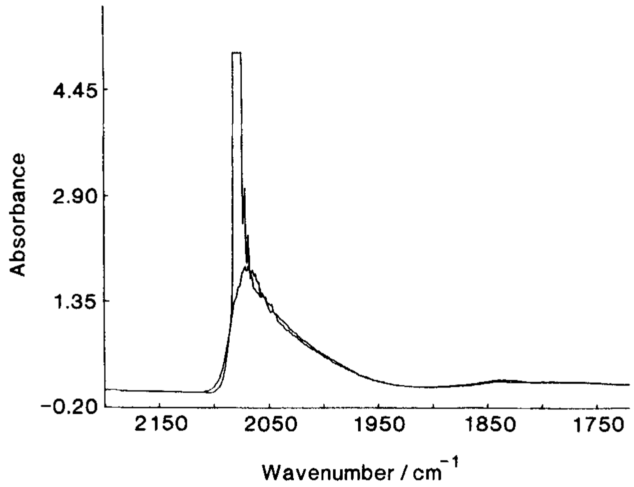

Figure 4. Infrared spectra of adsorbed CO on clean sample at full coverage.

Lower curve in H_2 residual pressure; higher curve shifted to high wavenumbers following evacuation.

which was calculated from the ratio of the integrated intensities of the linearly bonded band on the coked and clean samples.

Figure 5 shows the values of the integrated intensity of the CO absorption band for clean and coked samples. These values are calculated by integration of the absorption lineshape of the band in the range 1,900-2,125 cm^{-1} with a horizontal baseline. The apparent absorption intensity of the adsorbed CO is calculated from the slope of the straight line at coverage below one monolayer. A least-square linear regression gives a value of 35.01 cm^{-1} per μmol of adsorbed CO. For each sample, the chemisorption values in Table 2 are calculated by dividing the value of the total intensity at full coverage in the presence of a residual pressure of dihydrogen by the apparent absorption intensity.

As more CO is adsorbed, its absorption band maxima shift as shown in Figure 6. Coverage by CO is calculated by normalizing total absorbance to that at full coverage in the presence of a residual pressure of H_2. There is a distinctive behavior for both samples. For two samples of the clean sample, the band maximum is at 2,054 ($\pm$2) cm^{-1} at coverage below 0.1, but shifts steadily to slightly higher wavenumbers (6 cm^{-1}) with increasing coverage up to 0.9. The band maximum is at 2,067 ($\pm$2) cm^{-1} at full coverage in the presence of H_2, and it shifts up to 2,077 ($\pm$2) cm^{-1} following evacuation at RT. On the other hand, for two samples of the coked sample the band maximum is at 2,004 ($\pm$2) cm^{-1} at below 0.1 and then shifts linearly with coverage to higher wavenumbers up to 2,041 ($\pm$2) cm^{-1} at coverage higher than 0.8. There is no shift in the band following evacuation at RT.

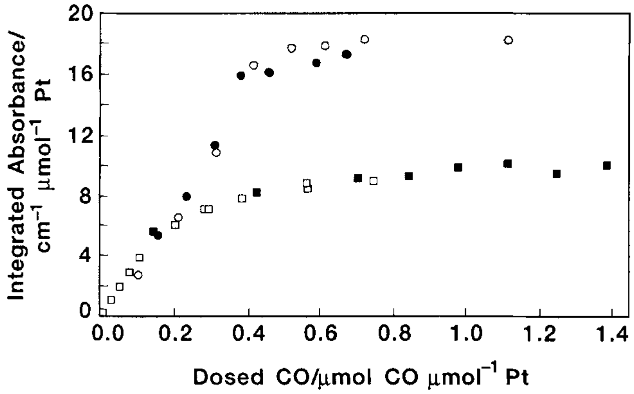

Figure 5. Intensity of the absorption band of adsorbed CO with increasing doses of CO.

◆ and ◇, clean sample; ■ and □, coked sample.

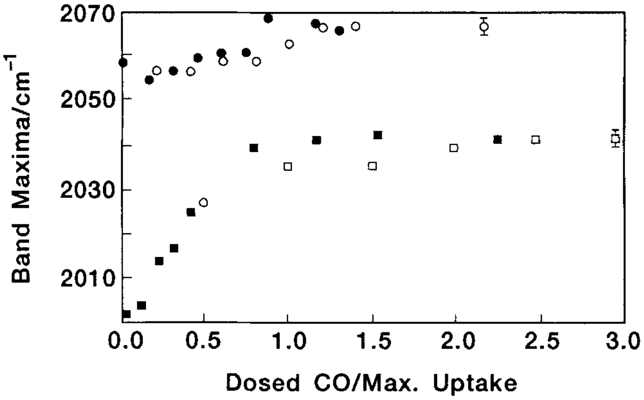

Figure 6. Maxima of absorption band of adsorbed CO with coverage.

◆ and ◇, clean sample; ■ and □, coked sample.

Discussion

Fraction of platinum surface exposed

A major concern in the interpretation of the H_2 titration is that the titration on the coked catalyst might overestimate the fraction of exposed Pt surface. Indeed, Davis et al. (1982) have shown that carbonaceous species release large amounts of H_2 between RT and 373 K. This could explain the observation reported in the Results section that while the hydrogen backsorbed at RT is 67% of the chemisorbed H on the clean Pt surface, it becomes 83% of the chemisorbed H on the coked Pt. This observation, however, can also be explained on the basis that the heat of adsorption of H_2 is less for the Pt covered with carbonaceous species than for clean Pt. This is supported by the observation that the binding of hydrogen is reduced by 8-12 kJ·mol^{-1} when co-adsorbed on Pt in the presence of hydrocarbon residues (Davis et al., 1982).

The analysis of the data from the adsorption isotherms of CO on clean Pt in both the absence and presence of a residual pressure of H_2 shows explicitly (see Figure 1) that one molecule of CO displaces one atom of adsorbed H on platinum at RT as explained in the Results section. The values for full coverage of CO (0.51 μmol CO/μmol Pt) and full coverage of H (0.70 μmol H/μmol Pt) indicate that some residual adsorbed hydrogen is not removed by carbon monoxide at RT. The ratio of the chemisorbed values for full coverage of carbon monoxide and hydrogen (0.51/0.70 = 0.73) is in good agreement with the values obtained by Benson and Boudart (1965) on Pt/Al_2O_3.

To calculate the amount of CO chemisorbed irreversibly on the coked sample (0.24 μmol CO/μmol Pt, see Table 2) it is assumed that 17% of the adsorbed H at RT is irreversibly chemisorbed. One can argue that this assumption might not be correct if some H_2 is reversibly chemisorbed on the carbonaceous species at RT. However, the estimated amount of CO irreversibly chemisorbed on the coked sample becomes 0.27 μmol CO/μmol Pt, if it is assumed that 33% of the adsorbed H on the Pt surface at RT is irreversibly chemisorbed on the coked catalyst as it is on the clean catalyst. Hence, the possible effect of the carbonaceous species on the adsorption isotherm does not alter the result that about 50% of the platinum surface is exposed on the coked sample.

Infrared spectroscopy of adsorbed CO is a very direct technique to calculate the fraction of surface Pt since it measures directly the infrared absorption intensity of CO. Moreover, the position of the absorption band indicates that CO is most linearly bonded on both the clean and coked sample so that a single adsorption stoichiometry seems warranted.

As presented in the Results section, the underlying assumption is that the integrated intensity of the absorption band in the range 1,900-2,125 cm^{-1} is directly proportional to the number of adsorbed molecules of CO. Indeed, as shown in Figure 5, the integrated intensity first increases linearly with increasing dosed CO. The slope of the line decreases at high coverage of CO for the coked sample as expected since a residual pressure is needed to get full coverage in the interval between doses (0.25-0.5 h). However, the clean sample shows a different behavior since the line curves in the upward direction, as befits an increase in the apparent absorption intensity per CO molecule above 0.7-0.8 of a monolayer. A similar deviation from linearity, although more intense, has been reported by Eischens and Pliskin (1958) in experiments where adsorbed CO is removed from a Pt surface by reaction with pulses of O_2 at 470 K. These authors explain this observation on the basis of strong interactions of adsorbed CO molecules at high coverage (≥ 0.66). The difference between these findings and our results can be explained if the adsorbed H present in our case weakens the interactions between CO molecules. Indeed, an increase of about 33% in the total absorbance of the band is observed when the catalyst is evacuated at RT after a monolayer of carbon monoxide is reached (see Figure 4). An observed blue shift in the band maxima position of 10 (± 2) cm^{-1} up to 2,078 (± 2) cm^{-1} is typical of strong dipole-dipole interactions of densely packed CO. In spite of the deviation of the integrated intensity per adsorbed molecule of CO at high coverage, the calculated value for the chemisorption of carbon monoxide (0.52 μmol CO/μmol Pt in Table 2) agrees with the value from the adsorption isotherms calculated for CO irreversibly chemisorbed on the clean catalyst (0.51 μmol CO/μmol Pt in Table 2). Again, it appears that adsorbed H weakens the coupling interaction of adsorbed carbon monoxide so that the integrated intensity per CO molecule remains essentially constant. The conclusion here is that the infrared absorption spectrum of adsorbed carbon monoxide on platinum at full coverage and in the presence of a residual pressure of H_2 at RT can be used to measure the number of molecules of adsorbed CO per platinum atom.

In summary, selective chemisorption methods indicate that about 50% of the surface platinum atoms remains exposed following hexane hydrogenolysis under the reported conditions. The methods are based on two independent data collection techniques: adsorption isotherm measurements and FTIR transmission spectroscopy, and two different gases—H_2 and CO. As the three methods give the same values for the fraction of surface Pt atoms exposed (about 50%), the uncertainties of these methods, described in the Introduction section, do not seem to play a noticeable role in this particular case.

Ethylene Hydrogenation of Coked Platinum Surfaces

The nature of the active sites for hydrogenation of ethylene on platinum has been discussed for a long time. Following the proposal by Zaera and Somorjai (1984), the reaction does not take place on the clean metallic surface but rather *on top of a layer of reactive carbonaceous fragments*, consisting of adsorbed ethylidyne. This suggestion is based on rate measurements on Pt (111) between 300-370 K. The authors detected a partially ordered carbon covered surface following ethylene hydrogenation. Their reported value for the turnover rate will be discussed later.

The formation of *unreactive* carbonaceous deposits on the metal surface during hydrogenation of ethylene was first proposed by Beeck (1950), who suggested that a parallel reaction is responsible for the formation of these species with the result of *poisoning* of the surface by acetylenic residues. This side reaction involving self-hydrogenation of ethylene to acetylene is probably very slow at very low temperatures, especially on platinum.

Indeed, Hattori and Burwell (1979) have shown that only a very small concentration (≤ 0.04 C_2/Pt_s) of slowly reacting "carbonaceous residues" is formed on platinum when a series of pulses of ethylene and H_2 are injected into flowing H_2 passing over a platinum-silica catalyst at both 242 K and 195 K. These authors suggest that platinum is the active phase for the reaction. Under their conditions, ethylene is adsorbed on the surface of the platinum to form a *reactive* monolayer that reacts sequentially with two $H\text{-}Pt_s$ and desorbs as ethane.

On the other hand, Thomson and Webb (1976) have proposed that the active site for hydrogenation reactions on metals is an adsorbed olefin (that is, olefin-metal complex) whose role is that of hydrogen transfer to the adsorbed hydrocarbon. In a way, their unspecified complex may be identified with the ethylidyne of Zaera and Somorjai.

The results of our work show that carbonaceous deposits formed during hydrogenolysis of *n*-hexane are actually poisoning the active phase of platinum for ethylene hydrogenation in direct proportion to the decrease of platinum surface exposed as measured by gas chemisorption methods.

Experimental Studies

The rate of ethylene hydrogenation was measured on a 5% $Pt\text{-}Al_2O_3$ catalyst before and following hexane hydrogenolysis. All the experiments were performed *in situ* (without exposing the sample to air between experiments). Detailed descriptions for the preparation of the catalyst and the hexane hydrogenolysis reaction are given in the preceding section.

The conversion of ethylene to ethane was measured as a function of time for both the clean and coked catalysts in a Pyrex batch recirculation system similar to the one reported by Schlatter and Boudart (1972). A small amount of catalyst (40-50 mg) was used in each run. The reduced catalyst (see above) was cooled down in H_2 to reaction temperature (192 K). The catalyst was evacuated under 1-5 mPa, and helium was introduced in the reactor up to atmospheric pressure. The composition of the initial reaction mixture was 3.1 ($\pm$0.1) kPa of ethylene, 20.3 ($\pm$0.3) kPa of H_2 and 78 ($\pm$1) kPa of helium. The conversion was less than 0.06 at the end of the measurement. The temperature changed by less than 1 K during any run, and there was a temperature variation of $\pm$2 K between runs. The product analysis was done in a gas chromatograph (HP 5980) with a flame ionization detector coupled with an integrator (HP 3600). A 2.5-m-long, 3-mm-diameter Chromosorb 102 column was used. A detailed description of the apparatus and procedure can be found elsewhere (Rivera-Latas, 1986).

Research-grade ethylene (99.99%, Matheson) was further passed through dehydrated 5A molecular sieve at Dry-Ice acetone temperature and MnO/SiO_2 at RT; in addition, several freeze-evacuation-thaw cycles were done before any rate measurement. Dihydrogen and helium were the same as described in the preceding section.

Results

The rate measurements of ethylene hydrogenation on the clean and coked catalyst indicate that 45% of the Pt surface atoms are exposed following hexane hydrogenolysis under the conditions of the preceding section. Table 3 shows the turnover rate for ethylene hydrogenation for both the clean and coked catalysts at 192 K, 3.1 kPa of ethylene, 20.3 kPa of H_2 and 78 kPa of helium. The actual kinetic data were always extrapolated to these conditions by assuming an activation energy of 38 $kJ \cdot mol^{-1}$, first order in H_2, and zeroth order in ethylene (Schlatter and Boudart, 1972). *The turnover rate is defined as the number of molecules of ethane produced per second and per exposed platinum atom as measured by titration of preadsorbed O by H_2 on the clean sample.* The ratio of the turnover rates is given in the third column (0.45). This value represents the fraction of surface platinum atoms exposed following hydrogenolysis of hexane.

The turnover rate is calculated from a plot of number of turnovers, N, vs. time, t (see Figure 7). The number of turnovers is defined as that of molecules produced per exposed platinum atom; it is determined from the conversion assuming a number of exposed Pt atoms as calculated by the O-H_2 titration on the clean catalyst. For the clean catalyst, the initial data, obtained before the number of turnovers reached unity, exhibited a decrease in the slope of the curve N vs. t. This variation depended on the residual pressure of H_2: the decrease in the slope was smaller in those runs where the catalyst was evacuated under pressure about 10^{-3} Pa before introducing helium in the reactor. For the coked catalyst, an activation period was observed before the reaction took off. These observations were not taken into account in the determination of the turnover rate since the kinetic steady state has not been reached on the surface before N has reached at least unity. The turnover rate is calculated from the slope of the linear portion of the plot which was obtained after N reached unity (Figure 7).

Table 3. Fraction of Platinum Surface Exposed from Rate Values for Ethylene Hydrogenation

	Turnover Rate* $v_t/10^{-2}\ s^{-1}$		Fraction of Pt Surface Exposed
5% Pt/γ-Al_2O_3-0.9% Cl	Clean	Coked	Coked
Ethylene Hydrogenation	1.28	0.58	0.45

*Turnover rate measured at 192 K, 20.3 kPa H_2, 3.1 kPa C_2H_4, and 77 kPa He.

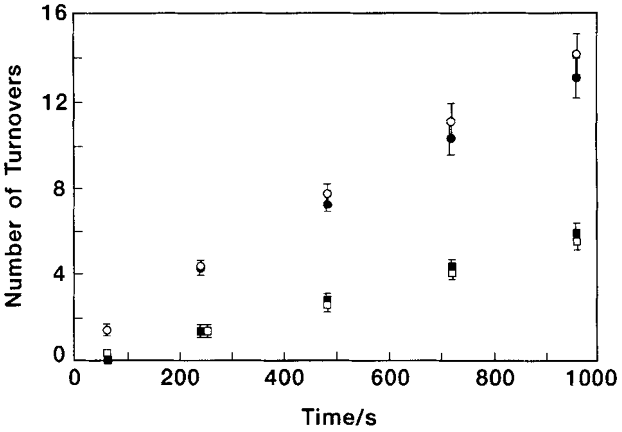

Figure 7. Number of turnovers vs. time for ethylene hydrogenation on both clean and coked catalyst (192 K, 3.1 kPa ethylene, 20.3 kPa dihydrogen, and 77 kPa helium).

The number of turnovers is based on the atoms at platinum surface counted by titration of pre-adsorbed O by H_2 on the clean catalyst. ◆, First run on the clean catalyst; ◇, second run on the clean catalyst; ■, first run on the coked catalyst; □, second run on the coked catalyst.

Discussion

The ratio of the rates of ethylene hydrogenation on platinum covered with carbonaceous species and clean platinum provides an independent measurement of the exposed platinum surface on the coked platinum. The rate is proportional directly to the fraction of surface platinum atoms exposed. In other words, the adsorbed carbonaceous species are actually poisoning the platinum surface in direct proportion to their surface coverage, as expected for a structure insensitive reaction (Leclercq and Boudart, 1981).

Figure 8 shows an Arrhenius plot of the turnover rate (v_t/s^{-1}) for ethylene hydrogenation on platinum. This result shows good agreement of our rate measurement with the turnover rate for platinum-evaporated film and platinum supported on silica and alumina, 0.5-5% platinum loading, and in the 175-273 K temperature range.The slope of the straight line corresponds to an activation energy of 39.5 $kJ \cdot mol^{-1}$, which agrees with the reported value of 38 $kJ \cdot mol^{-1}$ (Schlatter and Boudart, 1972). The good Arrhenius behavior for v_t with platinum loading varying *by a factor of ten* is the convincing proof of the absence of mass- and heat-transfer limitation in the rate measurements (Koros and Nowak, 1967; Madon and Boudart, 1982). No support effect can be seen in the data shown, encompassing unsupported Pt as well as Pt supported on silica and alumina.

The values of the fraction of surface platinum atoms exposed (0.45) are in excellent agreement with those calculated by selective gas chemisorption methods (Table 4). This is the most

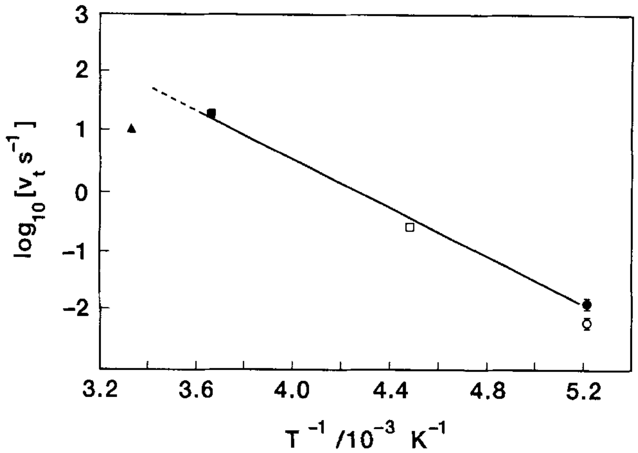

Figure 8. Arrhenius plot for ethylene hydrogenation on platinum.

v_t/s^{-1} is the turnover rate. ◆, 5% Pt/γ-Al_2O_3 (clean), this work; ◇, 5% Pt/γ-Al_2O_3 (coked), this work; ■, Beeck's Pt evaporated film, Schlatter and Boudart (1972); □, 0.5% Pt/SiO_2, Schlatter and Boudart (1972); ▲, Pt(111), Zaera and Somorjai (1984).

significant result of this work. Since the four methods used are independent, we are confident about the reported degree of contamination by carbonaceous species.

Our observations are compatible with the mechanism proposed by Zaera and Somorjai (1984) or the one proposed by Thomson and Webb (1976), provided that the adsorbed reactive hydrocarbon is associated with free platinum and not with coke formed during hexane hydrogenolysis. Our results agree with the idea that platinum atoms are the active sites for the reaction as proposed by Hattori and Burwell (1979) and Beeck (1950), while carbonaceous species poison the surface by blocking access to Pt atoms.

Platinum is very sensitive to poisoning by acetylene at the normal conditions for ethylene hydrogenation. This might explain the scattering of the turnover rates described by Schlatter and Boudart (1972). Because of high turnover rates, experiments are done with very small amounts of exposed platinum ($\leq$5-10 μmol Pt), and parts per million of acetylene might completely poison the platinum surface in flow reactor experiments after a few minutes of reaction. This is also true in the case of single crystal work even with the recirculation technique, since the amount of platinum exposed is extremely low ($\leq$3 μmol Pt). In the experimental work described here, the ethylene had 45 ppm of acetylene. Then, the number of molecules of acetylene in the reactant mixture is equivalent to 1-2% of the exposed platinum atoms in the clean catalyst since the recirculation system had a volume of 1,900 cm^3, and the partial pressure of ethylene was 3.1 kPa. In a single crystal work, those traces of acetylene in the ethylene could be equivalent to more than 100% of the platinum surface even for a recirculation volume as small as 200 cm^3.

Table 4. Fraction of Platinum Surface Exposed from Selective Gas Chemisorption and Rate of Hydrogenation of Ethylene

	Fraction of Pt Surface Exposed on the Coked Catalyst
Titration of Adsorbed Oxygen by Dihydrogen	0.56
Irreversible Chemisorption of Carbon Monoxide	0.48
FTIR Spectroscopy of Adsorbed Carbon Monoxide	0.50
Ethylene Hydrogenation	0.45

Figure 8 shows the value of the turnover rate for ethylene hydrogenation on single crystals of Pt(111) extrapolated to the conditions of this work from the value reported by Zaera and Somorjai (1984) ($v_t = 7.95\ s^{-1}$) at 300 K, 10 torr C_2H_4, and 100 torr D_2 (1 torr = 1.31 mbar). For calculating the extrapolated value, it was assumed that the reaction orders in ethylene (−0.6) and dihydrogen (1.3) partial pressures were used as proposed by those authors. Then, the turnover rate was multiplied by 1.3 to take into account the deuterium kinetic isotopic effect. The extrapolated turnover rate is a factor of ten lower than the value expected from Figure 8 from the experiments on supported catalysts and evaporated film, both at lower temperatures. This indicates that the rate for ethylene hydrogenation on Pt(111) may have been measured on a highly contaminated surface, either because of traces of acetylene in the reactant mixture or, more probably, formation of acetylenic species on the platinum surface from a secondary reaction involving self-hydrogenation of ethylene which might become important at the higher temperature of the single crystal experiment (300 K vs. 192 K in the present work).

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