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Kinetics of ethylene oxidation on plane Pt / SiO_2 catalysts in the viscous pressure regime: evidence of support activity

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C_2H_4 oxidation on plane Pt/SiO_2 model catalysts with various Pt loadings was studied at $T = 373$–473 K and in the pressure ranges 10^{-6}–10^2 Torr C_2H_4 and 0.3–1500 Torr O_2 (1 Torr = 133.3 Pa). Mass spectrometry combined with spatially resolved gas sampling enabled kinetic data to be collected far into the viscous pressure regime. Reaction orders and activation energies were similar to those of a macroscopic Pt surface. However, under fuel-lean conditions the global reaction rate decreases faster than the decrease in metal area. On the other hand, the global rate was *independent of Pt loading* and metal surface area in fuel-rich gas mixtures. This is interpreted in terms of a spillover effect.

Keywords: ethylene oxidation; platinum; silica-supported catalyst; spatially resolved gas sampling; transmission electron microscopy; support activity; spillover

1. Introduction

The interaction of ethylene (C_2H_4) with metal surfaces has attracted much attention throughout the years, due to the importance of C_2H_4 in industrial catalysis [1]. The specific interest in catalytic oxidation of C_2H_4 on Pt is primarily related to the global need to decrease the hydrocarbon content in car exhaust. Various aspects of this reaction have been studied in ultra-high vacuum (UHV) on single crystal surfaces [2–4] and at higher pressures on polycrystalline surfaces [5–16] as well as on supported catalysts [17–28]. Many studies have not focused on the reaction kinetics, but rather on associated phenomena such as rate oscillations [6,7,25,26,28], etching/sintering [10,11,23] or carbon overlayers [12,13]. In other cases, the C_2H_4 oxidation has mainly been used as a model reaction for demonstration of experimental techniques or evaluation methods [8,9,14,21,22,24]. The available kinetic data at near-atmospheric pressures are tabulated in ref. [16].

Recently, we studied C_2H_4 oxidation on a polycrystalline Pt foil and on plane, SiO_2-supported Pt films over a large pressure range [16], using the "spatially resolved gas sampling" (SRGS) technique [16,29]. Briefly, we found that (i) no structure sensitivity could be seen despite a varying microstructure of the samples, (ii) the reaction rate has a more complicated dependence on C_2H_4 and O_2 pressures than previous studies have indicated, and (iii) the rate data can be qualitatively fitted to a simple Langmuir–Hinshelwood (LH) model, assuming competitive adsorption of C_2H_4 and O_2, abundant molecular desorption of the excess reactant, and a strong self-inhibition of C_2H_4 adsorption.

Despite that most previous studies of C_2H_4 oxidation have been done with supported catalysts, the role of the support has never been discussed. Supports such as silica or alumina take active part in many catalytic reactions, some of which even involve C_2H_4 as a reactant, as proven by numerous studies on spillover phenomena [30,31]. Furthermore, silica can be made active for ethylene hydrogenation even in absence of catalytic metals [32–34].

This paper presents an extension of the prior work on macroscopic surfaces [16]. We have made plane models of Pt/SiO_2 catalysts by evaporating monolayer amounts of Pt onto oxidized silicon wafers. This gives separated Pt crystallites of nanometer size, thus resembling "real" silica supported catalysts. The $C_2H_4 + O_2$ reaction on these samples has been compared with previous data on dense Pt films over several orders of magnitude in pressure. Reaction orders and apparent activation energies do not differ significantly, but the reaction on SiO_2 supported Pt seems to proceed at comparable rates both on the metal islands and on the support in ethylene-rich gas mixtures. In excess of oxygen, on the other hand, the support activity is low. Since no activity is observed on a bare SiO_2 support, regardless of reactant mixture, we ascribe the SiO_2 activation to a spillover effect. In a recent UHV study [35] involving the same type of substrate, spillover phenomena were suggested to explain the kinetics of the $H_2 + O_2$ and $CO + O_2$ reactions on Pd/SiO_2.

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2. Experimental details

2.1. Sample fabrication

Experimental details on the fabrication and characterization of the SiO_2-supported, 100 nm thick, dense Pt films, referred to as "the films", were given in the preceding paper [16]. The Pt/SiO_2 model catalysts were fabricated according to a similar procedure [36]. The substrates were made by oxidation of 0.4 mm thick, polished silicon wafers in dry O_2 at 1473 K for 20 min, which gives a 100 nm thick, amorphous SiO_2 layer. Pt was deposited onto room-tempered substrates by electron-gun evaporation in a UHV chamber. Three samples with nominal Pt layers of 0.5, 0.08 and 0.02 nm, equivalent to about 2, 0.4 and 0.1 Pt monolayers, were made. The Pt thickness was monitored during deposition with a quartz crystal microbalance. There is a large uncertainty (possibly ± 0.02 nm) in the thicknesses, because the evaporation equipment is not optimized for submonolayer depositions. One reference sample without Pt, the "0 nm" sample, was also prepared. All samples were cut into 14×14 mm^2 pieces after fabrication, but otherwise used in reaction studies as received from the evaporation chamber.

Special samples for transmission electron microscopy (TEM) were also fabricated. They consisted of 0.08 nm Pt on a micromachined SiO_2 window, suspended in a silicon frame [37]. The growth of SiO_2 and the metal deposition were performed as described above. The SiO_2 window was thin enough ($\sim$ 100 nm) to make TEM studies possible without further sample treatments. The TEM samples were not fabricated on the same occasion as the other samples. Similar samples have been used previously for TEM studies of thicker Pt layers ($>$ 1 nm) [37–39].

2.2. Sample cleanliness

A separate Auger electron spectroscopy (AES) system was used for surface analysis of fresh samples and of samples used in several reaction studies. All features in the AE spectra could be attributed to SiO_2 or Pt, except for a carbon signal. C was found in similar amounts on fresh and on used samples, even on the 0 nm sample, and it was easily removed by argon sputtering; we therefore believe the contamination occurs during the sample transfer to the AE spectrometer, rather than during the reaction studies. The SiO_2 peaks dominated all AE spectra and they kept the same intensity upon argon sputtering, which indicates that all samples have a large fraction of bare SiO_2. The order of the Pt signal intensities of the 0.5, 0.08, 0.02 and 0 nm samples followed the order of the nominal amounts of Pt. The AE spectra of fresh and used samples were very similar. The Pt signals were slightly reduced for some used samples, however, possibly indicating a decrease of the metal dispersion.

2.3. Transmission electron microscopy

The TEM samples were cut to 3 mm diameter and imaged in a 400 kV high resolution electron microscope, capable of 0.16 nm point resolution. Since the Pt particles are situated on top of a 100 nm thick amorphous SiO_2 film, the contrast is very weak, and only in rare cases could single sets of the d_{111}-spacing (0.226 nm) of Pt be resolved. Judicious choice of focus is thus needed, as particle diameters in the here occurring size range are easily overestimated. To acquire true atomic structure images of Pt crystals of 0.6–30 nm size, a profile view without any amorphous background must be recorded [40]. Magnification calibration was instead performed on the crystalline Si edge surrounding the SiO_2 windows.

2.4. TEM image processing

To visualise the Pt particles and quantify the size and distribution, image processing was used. Typical areas were selected from the negatives from the microscope and digitised through a CCD video camera to a $512 \times 512 \times 8$ bit resolution. The magnification was chosen to correspond to 0.91 Å/pixel. A soft-edge passband filter, ranging from 5 to 125 pixels was applied in the Fourier plane of the image to eliminate varying illumination and shading from the optics of the CCD camera, and spatial frequencies higher than 0.18 nm (noise). A light local gaussian filter was thereafter applied to smoothen the edges of the particles.

Particle counting and classification was performed on the filtered images by a locally developed routine, based on the SEMPER image processing software. Since the granularity of the SiO_2 film is of the order 0.2–0.5 nm, a discrimination of the smallest particles was performed by interactive thresholding of the pixel intensity. The lower limit was set to the point where a dramatic increase in irregular, evenly spaced small particles appeared, giving a minimum diameter of around 0.7 nm.

2.5. Reaction studies with SRGS

The apparatus for reaction studies and the SRGS method have been described before [16,29,41]. Briefly, the apparatus is an isothermal, continuous-flow microreactor, operated at near-atmospheric pressures and equipped with mass-spectrometric gas analysis. The SRGS method comprises (i) mapping of steady-state pressure gradients with a local gas sampling probe in a stagnant layer close to the catalyst surface, and (ii) evaluation of reaction rates and true surface pressures from the measured gradients.

All experimental parameters in this work were identical with those described in the study of macroscopic Pt surfaces [16]. The reactant gases were O_2 (99.998%),

C_2H_4 (99.95%) and, in a special experiment, H_2 (99.9996%). Ar (99.9997%) was used as a diluent in some experiments and CO_2 (99.998%) was used for pressure calibrations. Under reaction conditions, gradients were observed in the C_2H_4 pressure but never in the O_2 pressure. Four O_2 pressures, 0.3, 3, 150 and 1500 Torr (1 Torr = 133.3 Pa), were used. The *surface* C_2H_4 pressure was in the range 10^{-6}–100 Torr and it was, as mentioned, often lower than the *nominal* C_2H_4 pressure.

A typical experiment was carried out as follows: A sample was continuously exposed to a fixed O_2 pressure and kept at a constant temperature between 373 and 473 K. An C_2H_4 pulse of known nominal pressure was applied and local pressures of C_2H_4, CO_2 and H_2O were measured as a function of distance from the sample. The pulse duration was normally a few minutes. This was repeated for several nominal C_2H_4 pressures, first for increasing and then for decreasing pressures, in order to ensure that a steady-state catalytic activity was reached. We did not pretreat the samples by gas exposures or heating before starting an experiment.

Just as in the previous study [16], linear pressure gradients were found within ~ 1 mm distance from the sample. By applying one-dimensional diffusion laws to the gradients, consumption rates, production rates and surface pressures could be extracted. The lowest detectable rate was in the range 10^{-8}–10^{-7} mol m^{-2} s^{-1}. We estimate that the C_2H_4 surface pressures are correct within ~ 20% as long as they do not fall below 1% of the nominal pressure [42]. Below 1%, the accuracy rapidly deteriorates. Such extreme C_2H_4 depletion was occasionally observed at low O_2 pressures or high temperatures and the corresponding, less accurate, data points are not included in the figures below.

All reaction rates and surface pressures in this paper are surface averages assuming a uniform catalytic activity all over the sample surface, despite that it is composed of both Pt particles and SiO_2 areas. These surface averages are justified by the fact that the gas-phase mean free path in this study (~ 40 nm or larger) is always larger than the characteristic dimension of the sample microstructure (1–10 nm). Sample areas of different catalytic activity will therefore experience the same reactant surface pressure for a given nominal pressure. The reaction rates, given in units of mol m^{-2} s^{-1}, are equal to global diffusion rates through a two-dimensional plane parallel with the sample surface, i.e. no corrections have been made for the microstructure of individual samples.

The terms "relative area" and "relative rate" used below are the metal area and the global reaction rate of a Pt/SiO_2 sample, expressed in percent of the area and rate of a dense Pt film sample.

SRGS thus provides true kinetic data for diffusion-controlled reactions. Experimental difficulties may arise in pressure regions where the rate derivative with respect to pressure is large and negative. A small change of the nominal reactant pressure may then induce a giant leap of the surface reactant pressure as the system switches between kinetic control and diffusion control [43]. This phenomenon is discussed in detail elsewhere [42]; it is, however, the reason for the lack of data near the rate maximum in some experiments shown below.

3. Results

3.1. Structural characterization

TEM studies were performed in order to determine Pt particle size and distribution and also to look for structural changes upon heating and gas exposure. Fig. 1 shows images of a fresh 0.08 nm TEM sample (fig. 1a) and of the same sample after exposure to $C_2H_4 + O_2$ at 423 K for 6 h (fig. 1b). Direct identification of Pt particles in these unfiltered images is difficult, due to the low contrast and the granularity of the SiO_2 window. Particles become visible, however, in the filtered images shown in figs. 1c and 1d. The used sample clearly has fewer and larger particles than the fresh sample. This is consistent with the reduced Pt intensity observed in AE spectra of used samples.

Table 1 gives some structural parameters obtained by an analysis of the filtered images. The mean particle sizes of the fresh and the used sample are about 1 and 2 nm, respectively. The amount of Pt on the used sample corresponds well with the nominal Pt thickness, if one assumes that the typical particle shape is between hemispherical and spherical. A similar calculation for the fresh sample yields a nominal thickness which is too low; some particles in the unfiltered image (fig. 1a) probably lack the contrast needed to survive the filtering process.

We conclude that a somewhat increased particle size is observed upon heating and gas exposure, but the particles are still very small (< 3 nm) on samples that have been used for hours.

3.2. Reaction studies: general observations

The 0 nm sample did not oxidize C_2H_4 at a detectable rate. All Pt/SiO_2 samples were active and the products were CO_2 and H_2O for all tested reactant mixtures, in accordance with the films [16]. Fig. 2 shows an example of the production of CO_2 vs. the consumption of C_2H_4. Substantial production of partially oxidized species should have shown up as a deviation from the observed proportionality in fig. 2. Production of minor amounts of CO cannot be excluded, however, since the mass spectrum of CO is severely overlapped by the spectra of CO_2 and C_2H_4.

An increasing activity was sometimes observed during the initial C_2H_4 pulses of an experiment with fresh as well as with used samples. Once steady state was reached, reaction rates were reproducible from one experiment to another. Thus it seems that the initial

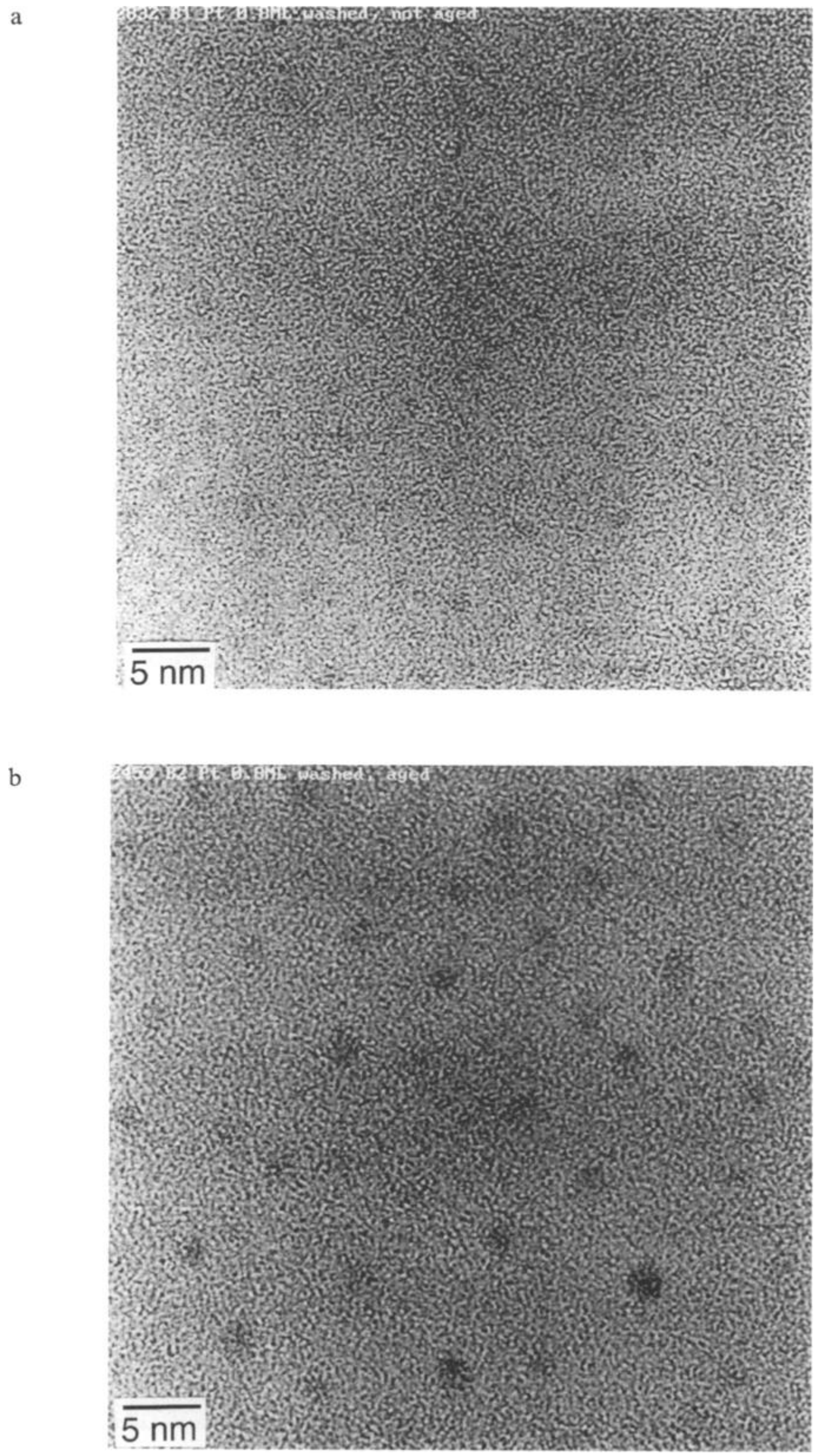

Fig. 1. (a) TEM image of a fresh 0.08 nm Pt sample. (b) TEM image of a 0.08 nm Pt sample exposed to reactants at $T = 423$ K for 6 h. The exposure consisted of a continuous flow of 150 Torr O_2, into which pulses of 13 Torr C_2H_4 were injected every 60 s. The pulse duration was 30 s. (c) Filtered image of the fresh sample. (d) Filtered image of the used sample.

activity increase is due to an activation of the surface. The dispersion change suggested by TEM (fig. 1 and table 1) and AES data was not evident in the reaction studies. This may indicate that the restructuring mainly occurs during the very first heating and gas exposure of a fresh sample.

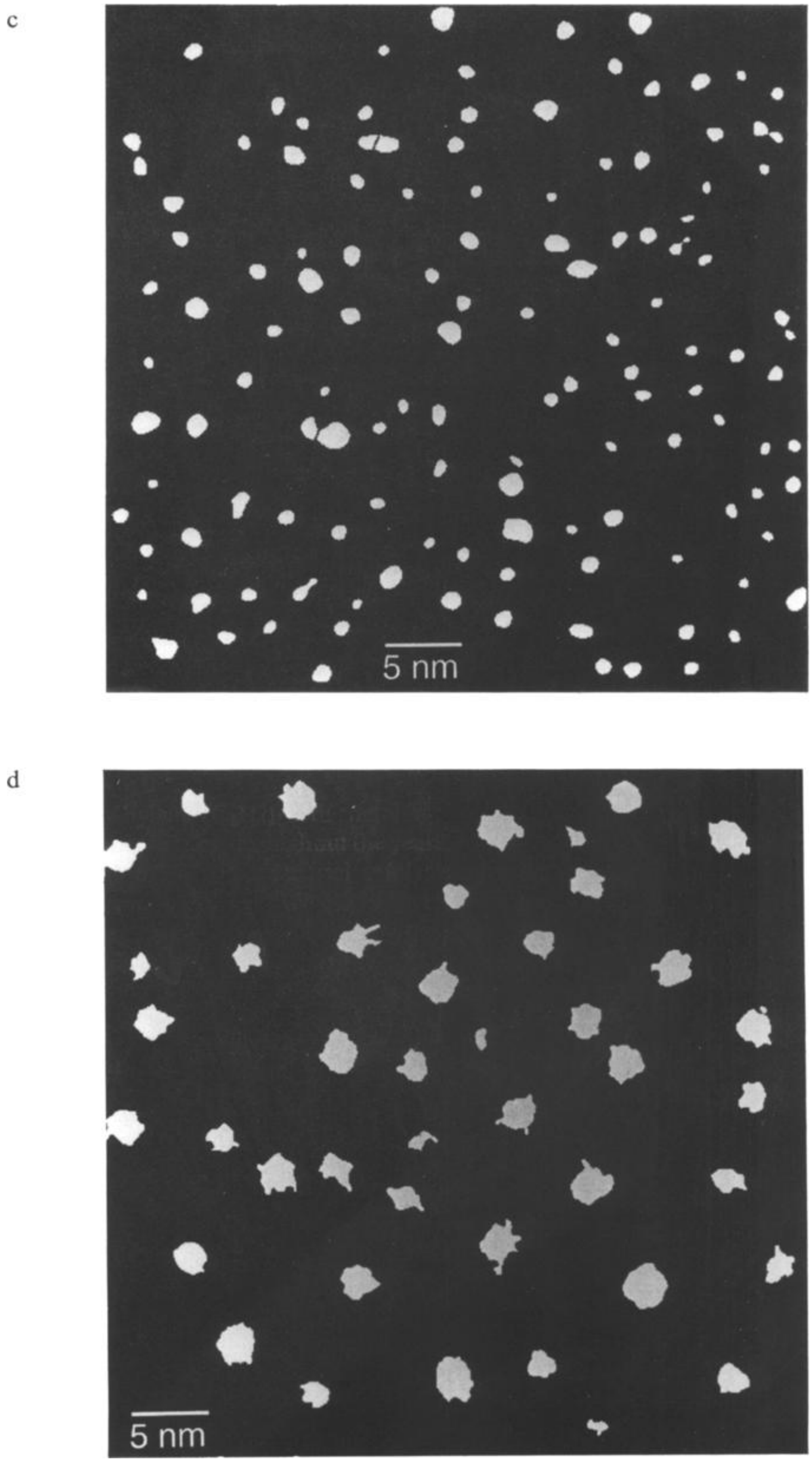

Fig. 1. (Continued.)

Independent groups have reported self-sustained oscillations in the C_2H_4 oxidation rate on Pt [6,7,20,25,26,28]. We never observed oscillations, neither in the preceding [16] nor in the present study. We believe that the inherent properties of the reactant/catalyst system itself are not sufficient to initiate oscillations; external parameters, e.g. surface contaminants or heat/mass transfer limitations, are also involved.

Table 1
Structural parameters of the 0.08 nm sample, calculated from the TEM images in figs. 1c and 1d

	Fresh sample	Used sample
image area	47 × 47 nm^2	47 × 47 nm^2
No. of counted particles	127	43
2-dim. coverage	5.1%	7.0%
min. 2-dim. diameter [a]	0.6 nm	1.0 nm
max. 2-dim. diameter [a]	1.9 nm	2.9 nm
mean 2-dim. diameter [a]	1.0 nm	2.1 nm
relative Pt area [b]	10% (hemispheres) 20% (spheres)	14% (hemispheres) 28% (spheres)
corresponding nominal Pt thickness [b]	0.02 nm (hemispheres) 0.04 nm (spheres)	0.05 nm (hemispheres) 0.1 nm (spheres)

[a] Calculated from individual particle areas, assuming circular particle shapes.
[b] Assuming that the particles are (hemi)spherical.

3.3. Rate vs. pressure dependence

Fig. 3a shows the CO_2 production rate vs. the C_2H_4/O_2 pressure ratio at $T = 423$ K for the 0.08 nm sample. At low ratios, the data converge towards a straight line of unity slope, implying reaction orders of +1 in C_2H_4 and −1 in O_2 in fuel-lean gas mixtures. The same reaction orders were observed for the 0.02 and 0.5 nm samples and also for the films [16]. Positive first order in C_2H_4 at low ratios has been reported previously [6–9,18,19,21,22], but it has never been confirmed over such a large pressure range. Mandler et al. [22] also suggested negative first order in O_2 in a study over less than one order of magnitude in O_2 pressure. In contrast, Vayenas et al. [6–9] found zero order in O_2 for porous Pt films.

A similar fit for fuel-rich gas mixtures is illustrated in fig. 3b. The reaction orders at high C_2H_4 pressures were −0.5 in C_2H_4 and +1 in O_2, for all Pt/SiO_2 samples as well as for the films [16]. Most previous works have indicated orders of −1 in C_2H_4 and +1 in O_2 [17,20,22], based on data collected in a narrow pressure region near the rate maximum. In fact, a steeper slope is seen near the rate maximum in fig. 3b, indicating a more negative reaction order in C_2H_4 under "slight" C_2H_4 excess.

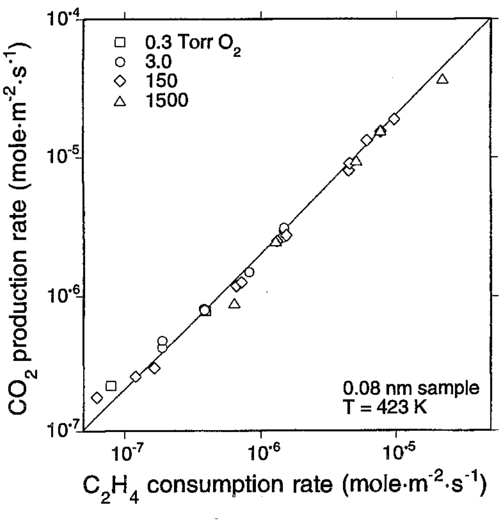

Fig. 2. CO_2 production rate vs. C_2H_4 consumption rate for a 0.08 um sample at 423 K. The C_2H_4 pressure was varied over seven decades (~ 10^{-6}–10 Torr), from fuel-lean to fuel-rich conditions. The line indicates the 2 : 1 proportionality expected from a complete oxidation to CO_2.

3.4. Rate vs. temperature dependence

The temperature dependence of the reaction rate was investigated for the 0.08 nm sample at 150 Torr O_2 and $T = 398$–448 K. *Apparent* activation energies were extracted from standard Arrhenius plots, obtained at various C_2H_4 pressures. Fig. 4 shows activation energies and reaction rates of the 0.08 nm sample compared with the film [16]. It is clearly seen that the *activation energies are almost identical for the two sample types* over the pressure range studied here, despite that the rate curves are quite different.

The apparent activation energy is strongly dependent on the experimental conditions since the variation in surface coverage with temperature is not explicitly accounted for in such calculations. In fig. 4, the surface coverage will vary drastically when going from low to high ethylene pressure. At low ethylene pressures it is likely that oxygen dominates on the surface while at high ethylene pressures ethylene derived species will dominate. Clearly, the apparent activation energy cannot be used as a "fundamental reaction parameter" if the experimental conditions are not very carefully specified. Literature data obtained with supported Pt catalysts in fuel-rich gas mixtures scatter between 77 and 102 kJ/mol [17,20–22], i.e. close to or above our *maximum* value. In the O_2 excess regime, activation energies as different as 31 kJ/mol [21] and 108 kJ/mol [22] have been reported. It should be added that most previous work has been done with Pt supported on Al_2O_3.

3.5. Rate vs. thickness dependence

A comparison of the reaction rates for different nominal Pt thicknesses (fig. 5) reveals some interesting fea-

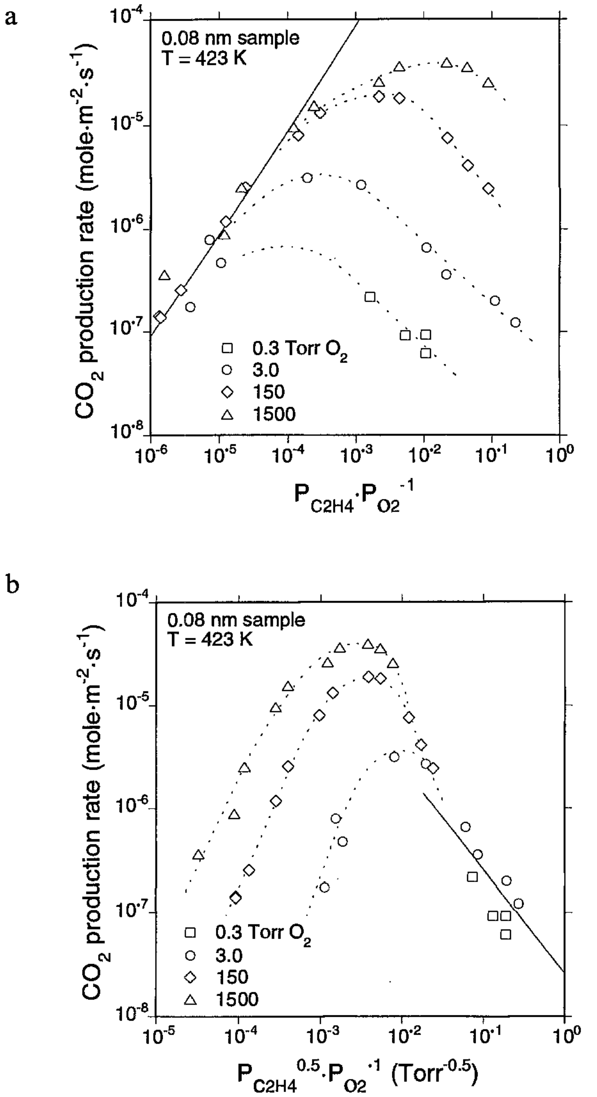

Fig. 3. Evaluation of reaction orders for a 0.08 nm sample at 423 K. Dotted lines are only drawn as a guide to the eye. (a) CO_2 production rate vs. $P_{C_2H_4}P_{O_2}^{-1}$. The solid line indicates direct proportionality (slope = +1). (b) CO_2 production rate vs. $P_{C_2H_4}^{0.5}P_{O_2}^{-1}$. The solid line indicates inverse proportionality (slope = −1).

tures. In oxygen excess, the relative rates of the 0.5, 0.08 and 0.02 nm samples are about 20, 2.5 and 1%, respectively, of the rate of the film. A much weaker thickness dependence is found in C_2H_4 excess. These observations were independent of the absolute pressures and the temperatures used in this study. Fig. 6 shows the rate curves of the 0.08 nm sample and the film at 373 and 473 K. The relative rate of the 0.08 nm sample remains at 2.5% in fuel-lean mixtures, whereas the rates of both samples converge into almost a single curve under fuel-rich conditions.

In order to further explore this anomalous rate vs. thickness dependence, a 0.08 nm sample and a film were also subjected to a special experiment with H_2 as reactant instead of C_2H_4. Fig. 7 shows the H_2O production vs. H_2 pressure at 3.0 Torr O_2 and 423 K. In this case, the relative rate is 14% both in fuel-lean and in fuel-rich mixtures.

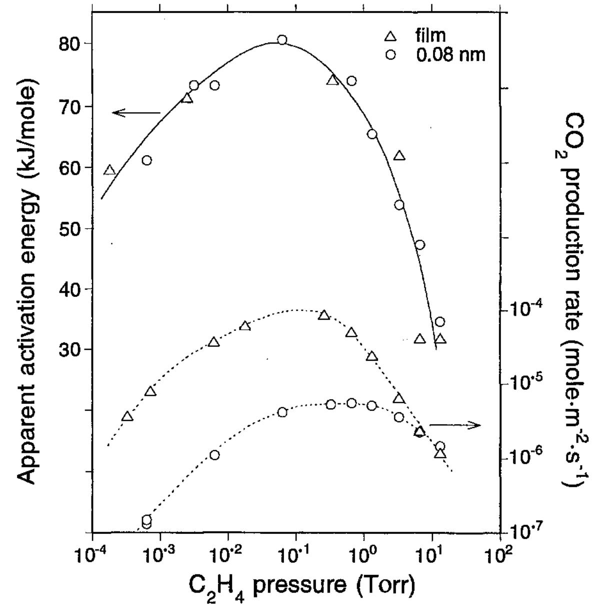

Fig. 4. Apparent activation energy and CO_2 production rate vs. C_2H_4 pressure for a film and a 0.08 nm sample at 150 Torr O_2. The activation energies were determined from rate measurements at $T = 373$–423 K for the film and at $T = 398$–448 K for the 0.08 nm sample. The CO_2 production rates shown were measured at 398 K. Lines are only drawn as a guide to the eye.

We have preferred to present the data in terms of absolute, global, reaction rates since this is what we measure. To obtain the rates as number of turnovers per second and Pt surface atom, the given numbers should in the case of the Pt film be multiplied by 2×10^4. The

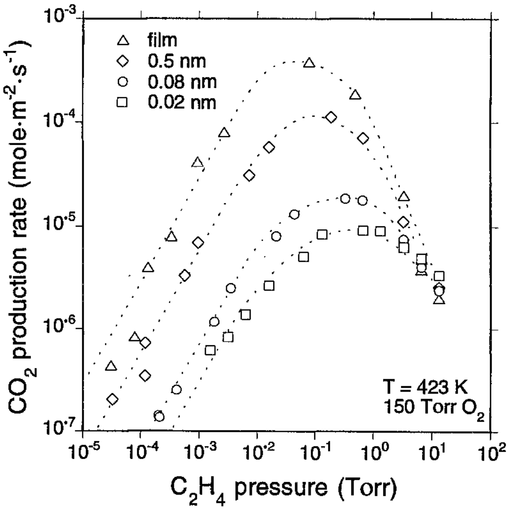

Fig. 5. CO_2 production rate vs. C_2H_4 pressure at $T = 423$ K for all sample types. The O_2 pressure was 150 Torr. Lines are only drawn as a guide to the eye. The reaction rates, given in units of mol m^{-2} s^{-1}, are equal to global diffusion rates through a two-dimensional plane parallel with the sample surface. By multiplying e.g. the film result with 2×10^4 and the 0.08 nm result by 1.4×10^5 the turnover frequencies, i.e. turnovers per Pt surface atom and second, are obtained.

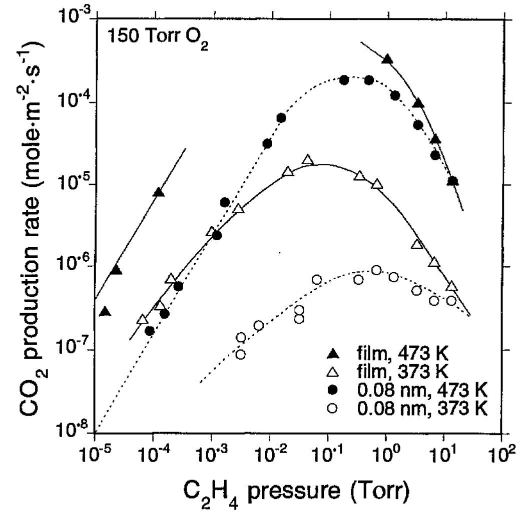

Fig. 6. CO_2 production rate vs. C_2H_4 pressure for a film and a 0.08 nm sample at 150 Torr O_2 and two different temperatures (373 and 473 K). Lines are only drawn as a guide to the eye.

maximum turnover frequency in, e.g., fig. 5 is thus around 6 s^{-1}. Using the relative rate from the H_2O production shown in fig. 7 as being representative of the surface area difference between a film and the 0.08 nm sample (see discussion below), the 0.08 nm rates of figs. 5 and 6 should be multiplied by approximately 1.4×10^5 in order to obtain turnover frequencies.

4. Discussion

In the preceding study of Pt films and foils [16], the results were discussed in terms of a simple, qualitative model involving competitive reactant adsorption, high surface coverages and significant desorption of reactants back to the gas phase. Since C_2H_4 oxidation on the supported Pt/SiO_2 catalysts shows the same qualitative behaviour as on the macroscopic Pt surfaces, i.e. the reaction products, the reaction orders and the activation energies remain unchanged, we believe that the reaction mechanisms are similar for both sample types. Thus the previous discussion [16] can be applied also to the present data. Here we will focus on the rate vs. Pt thickness dependence and its origin.

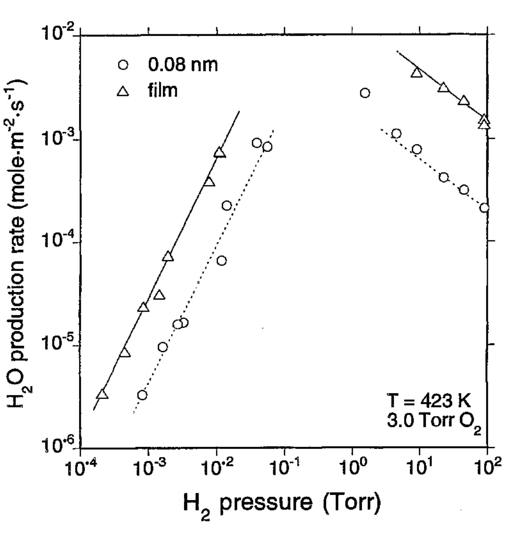

Fig. 7. H_2O production rate vs. H_2 pressure for the $H_2 + O_2$ reaction on a film and a 0.08 nm sample. The temperature was 423 K and the O_2 pressure was 3.0 Torr. Lines are only drawn as a guide to the eye.

4.1. Oxygen excess

Since the nominal Pt thickness on our Pt/SiO_2 model catalysts is two monolayers or less, it seems likely that they all have a lower Pt area than that of a thick, dense Pt film. This is also confirmed for the 0.08 nm sample by the TEM studies (fig. 1 and table 1). Thus, the simplest reason for the different reaction rates in oxygen excess would be that the metal areas are different. The 2.5% relative rate of the 0.08 nm sample is, however, not consistent with the relative area suggested by the TEM images (table 1). A better agreement with the TEM data is found in the $H_2 + O_2$ experiment (fig. 7), which gives a 14% relative rate *on both sides of the rate maximum.* We strongly believe that the latter is a better measure of the relative area.

In the case of C_2H_4 oxidation, we suggest that the relative rates of the Pt/SiO_2 catalysts are determined not only by the relative areas, but also by some structure-sensitive parameter which slows down the turnover frequency on small, single Pt crystallites. This appears contradictory to the structure insensitivity observed in the preceding study [16], but the previous samples were macroscopic, bulk-like Pt films and foils with grains much larger (10–1000 nm) than the Pt crystallites (< 3 nm) seen in fig. 1. It has been shown that single Pt particles of nanometer size do not exhibit the electronic structure characteristic of bulk Pt [44,45]. The structure sensitivity may thus be related either to the electronic properties of small particles or to the density of reaction sites on the particles. Carberry [18,19] observed an increasing turnover frequency with crystallite size when studying C_2H_4 oxidation on Pt crystallites on Al_2O_3 in fuel-lean gas mixtures, in agreement with our results.

4.2. Ethylene excess

The most remarkable observation in this study is that submonolayer amounts of Pt on a flat silica surface and a plane macroscopic Pt surface exhibit similar activities under fuel-rich conditions. Four possible explanations are discussed below.

(i) The reaction on Pt is structure sensitive

It can be argued that the reaction occurs on the Pt only, provided that the turnover frequency in the fuel-rich regime increases with decreasing Pt particle size. Such an argument is easily refuted if the global rate exceeds the rate of reactants impinging onto the Pt particles [35], but in our case the global rate is orders of magnitude below that limit. However, we find it very unlikely that a structure sensitive turnover frequency would compensate exactly for the lower metal area of the various Pt/SiO_2 samples as to always keep the global rate constant. Furthermore, previous studies [16,18,19] have indicated structure insensitivity in C_2H_4 excess.

(ii) The reaction proceeds on SiO_2

Another possibility is that SiO_2 itself catalyzes C_2H_4 oxidation at a rate comparable to that of Pt. It has been shown that pure silica, in absence of other materials, can be made catalytically active, e.g. by exposure to hydrogen plasma [32], by methoxylation [33] or even by long-term heating in argon [34]. Support activation by hydrogen spilt over from Pt to SiO_2 has also been demonstrated [46].

The zero activity of the 0 nm sample clearly shows that our substrates are not inherently active. Activation by hydrogen spillover seems more probable, since C_2H_4 oxidation indeed gives free hydrogen atoms on Pt in fuel excess [16]. Still, there is no reason why reaction orders and activation energies on SiO_2 should be the same as for a Pt surface. Moreover, reactions involving direct adsorption of O_2 on SiO_2 have, to our knowledge, never been reported. It is thus not likely that all reaction steps occur on the SiO_2 surface itself, even if it is spillover activated.

(iii) Reactant adsorption occurs on a spilt-over carbonaceous overlayer

Several investigators have shown that C_2H_4 *hydrogenation* on Pt is a structure insensitive reaction [1,47,48] and occurs in presence of a rather stable carbonaceous overlayer [1,47–51], but there is no consensus whether the overlayer poisons [48,49] or promotes [1,47,50] the reaction. Based on an idea of Thomson and Webb [50], Somorjai et al. [47] have argued that C_2H_4 is adsorbed and hydrogenated *on top of the overlayer* and, therefore, the structural details of the metal are not important. They have also proposed [1,51] that the working catalyst surface still contains ensembles of uncovered Pt sites with properties resembling a clean Pt surface. A carbonaceous overlayer must build up also during C_2H_4 *oxidation* in fuel-rich gas mixtures. The structure insensitivity observed on Pt films and foils [16] can thus be explained if the rate-limiting step occurs on the overlayer, in line with the Somorjai model.

An extension of the Somorjai model gives an attractive explanation to our present results. Assume that a carbonaceous overlayer forms on the supported Pt particles in C_2H_4 excess. If the overlayer readily spills over to the SiO_2 surface, while keeping its ability to mask the structure of the underlying surface, the working surface of a Pt/SiO_2 sample will appear very similar to that of a Pt film. Assume that the rate-limiting reaction step is the adsorption of reactants on the overlayer and that the reactants, once adsorbed, diffuse easily on this overlayer, while the role of the Pt particles is to provide a sufficient density of sites for dissociation or reaction. If the overlayer extends over the whole SiO_2 surface, the total sample area accessible to adsorption will be the same as for a macroscopic Pt surface, thus explaining why the global rates are similar for all sample types.

(iv) The substrate acts as a sink for carbonaceous species

An advantage of model (iii) above is that the density of uncovered Pt sites does not affect the reaction rate. In contrast to the Somorjai model, other workers [48,49] have proposed that the carbonaceous overlayer is a site-blocking poison and that the hydrogenation occurs on uncovered Pt sites only. If this is the case also for C_2H_4 oxidation, the density of uncovered Pt sites should be important. Can our observations in the C_2H_4-rich regime be explained by similar densities of vacant Pt sites on the working surface of all sample types, despite that the total densities of Pt sites are different?

If vacant sites on Pt are assumed to be randomly distributed, the answer is no. However, it has been suggested that vacant sites collect into patches in the carbonaceous overlayer [1,51]. Assume that the density and size of these patches on the working Pt film are smaller than the density and size of the Pt crystallites on the Pt/SiO_2 catalysts. Further assume that the crystallites and the substrate of a working Pt/SiO_2 catalyst are covered by a mobile carbonaceous overlayer, and that patches do not easily form in the substrate overlayer (e.g. due to lateral attraction between spiltover species). The Pt/SiO_2 catalyst and the Pt film will then exhibit very similar working surfaces; the only difference will be that on the macroscopic Pt surface the patches of vacant sites can move freely, whereas they are restricted to the Pt particles on the Pt/SiO_2 catalysts.

It should be added that a very small fraction of vacant sites would suffice for the observed reaction rates in C_2H_4 excess, provided that molecules impinging on the vacant sites react with a high probability. The reaction rate at the highest C_2H_4 pressure in fig. 5, for instance, corresponds to a *global* reaction probability of the order of 10^{-8} only. If the *local* reaction probability on vacant sites is $> 10^{-4}$, which is not an unreasonably high value, less than 0.01% of the whole Pt/SiO_2 surface need to consist of uncovered Pt atoms.

We favour models (iii) and (iv) above, i.e. we believe that carbonaceous species on the SiO_2 surface are important for the interpretation of our results. Is it possible for a carbonaceous overlayer to form on SiO_2 by direct adsorption/dissociation of C_2H_4? Low and Mark [33] and Bittner et al. [34] have indeed shown that C_2H_4 adsorbs, but they needed to pretreat their silica, either at very high temperatures (> 800 K) [33] or for many hours at somewhat lower temperatures (~ 600 K) [34]. As seen in fig. 6, our substrate seems active even at the lowest temperature tested (373 K). Since C_2H_4 readily adsorbs and dissociates on Pt, even at room temperature [1], we believe spillover is more likely than direct adsorption. In addition, our rate data in oxygen excess do not suggest any substrate activity, which is consistent with an activation by spillover of ethylene-related species.

Some support to the assumption that C_2H_4 (or dissociated fragments) interacts with silica is found in a recent IR spectroscopic study by Jackson et al. [52]. Upon exposure of a Pt/silica catalyst to C_2H_4 at room temperature, they observed changes in the bands associated with hydroxyl groups on the support. The nature of this interaction was, however, not clarified.

4.3. Final remarks

Whatever phenomenon causes all samples to give similar global rates in C_2H_4 excess, we are convinced that it cannot be ascribed to the properties of the Pt particles only; surface processes on the silica also contribute. We further believe that transport of some surface species between the Pt and the SiO_2, i.e. a spillover process, is needed to account for the observations. Obviously, we are far from understanding the details; more experimental data are certainly needed. The importance of the support can be further elucidated simply by repeating the present experiments with Pt supported on other substrate materials. Direct evidence of spillover species on a support can be obtained, e.g., by IR spectroscopic methods [53], by ellipsometry [54] or, as demonstrated recently, by a scanning light pulse technique [55]. Titration experiments in UHV may also provide information on spillover processes on plane model catalysts [35].

Finally, we wish to point out that our studies of spillover phenomena on plane metal/SiO_2/Si structures stem not only from a fundamental interest in catalysis but also from the fact that similar structures, in the form of field effect transistors, have been used as gas sensors for a long time [36]. Spillover processes have been shown to occur on these devices [36,54,55], but it is still unclear whether they are important for the sensing mechanism.

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