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The Role of Coke in Acetylene Hydrogenation on Pd/α-Al_2O_3

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The formation of coke and the influence of the coke on selectivity were investigated during hydrogenation of acetylene on supported palladium catalysts. It was found that the total amount of coke was not directly related to the increase in formation of undesired ethane. Instead, the surface coverage of hydrogen during the deactivation was found to be a crucial parameter. A catalyst deactivated at low hydrogen surface coverage showed a higher ethane selectivity than a sample deactivated at higher surface coverage of hydrogen when compared under the same reaction conditions. In contrast, the coke formation rate was found to increase with increased hydrogen surface coverage. The role of carbon monoxide was also investigated, and the impact on selectivity and coke formation was explained by the reduced surface coverage of hydrogen in the presence of carbon monoxide. The coke was characterized by temperature-programmed oxidation, and deconvolution of the obtained peaks was carried out using a power-law model.

INTRODUCTION

In the thermal steam cracking process, producing ethene and propene, acetylene is also formed. This impurity is removed in a selective hydrogenation process, which is usually performed on a supported palladium catalyst. An obvious objective in this process is to avoid hydrogenation of the ethene to ethane while reacting all but a few ppm of the acetylene. Modern catalysts are indeed very selective, at least in the presence of carbon monoxide, but the ethane formation is well known to increase with time on stream (1–3).

The mechanisms and kinetics involved, including the role of the selectivity promoter carbon monoxide, have received considerable attention in previous literature. Surveys of commercial processes and kinetics can be found in (1) and (4), respectively, while additional kinetic work is available, e.g., in Refs. (5–9).

In addition to hydrogenation, acetylene undergoes hydropolymerisation reactions, leading to liquid polymer mixtures ("green oils") and/or the deposition of carbonaceous species on the catalyst surface. Such liquid fractions have been found to consist of paraffins and olefins ranging from about C_8 to C_{24} with an H/C ratio of about 1.9 (10, 11). In industrial operation the coke formation results in a reduced overall activity as well as an increased selectivity for the undesired ethane (10). In laboratory experiments, normally performed at lower pressure, several groups have observed constant or even slightly increasing activity for about 100 h of operation (3, 8, 12, 13). Sárkány *et al.* (3) have presented a comprehensive study using different catalysts and conditions. In summary, they found ethane selectivity to increase with increasing coke formation on all supported catalysts. On unsupported Pd black and in the presence of CO, this effect was suppressed.

Several groups (2, 10, 20) report that the coke concentration decreases with increasing hydrogen pressure. Battiston *et al.* (2) found that the concentration of carbon on the catalyst increased with decreasing H_2/C_2H_2 ratio. However, with no hydrogen in the feed the coke formation was negligible. Sárkány *et al.* (3) varies the hydrogen surface coverage by having different CO concentrations in the gas feed but keeping the hydrogen partial pressure constant. They note that the C_4 formation goes through a maximum upon increasing CO concentration.

Asplund (14) has studied the effect of coke formation on the intraparticle mass transfer. Accumulation of large amounts of coke was found to block the catalyst pores and induce mass transfer limitations that could not be detected on a fresh catalyst. This phenomenon was found to be important even on a commercial catalyst of the eggshell type.

Asplund *et al.* (15) also studied deactivation of a monolithic catalyst in different gas mixtures and in the presence of an organic liquid phase. Catalyst aging in a hydrogen-rich atmosphere ($H_2/C_2H_2 = 4.5$) gave rapid coke formation and an increasing ethane selectivity. The catalyst performance was easily restored by oxidation in air at 573 K. When catalyst aging was performed in the presence of a liquid

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phase (*n*-heptane) the coke accumulation was almost completely stopped but the ethane selectivity still increased. Further, catalyst performance could not be restored even by oxidation at 743 K. It was concluded that the effect of coke on selectivity is caused by highly unsaturated species, whose formation is suppressed by a high enough hydrogen excess.

The present work aims to clarify further the relation between operating conditions, coke composition, and the effect of coke on catalyst performance. The idea is to first deactivate the catalyst in different gas-phase conditions (different partial pressures of H_2, C_2H_2, and CO). Thereafter the catalyst performance (i.e., ethane selectivity) is measured at a standard gas-phase composition. The influence on the selectivity of different reaction conditions is thus eliminated and the deactivated catalysts are evaluated under equal conditions. Temperature-programmed oxidation (TPO) and desorption (TPD) are used to study the coke accumulated on the catalyst surface (16–18).

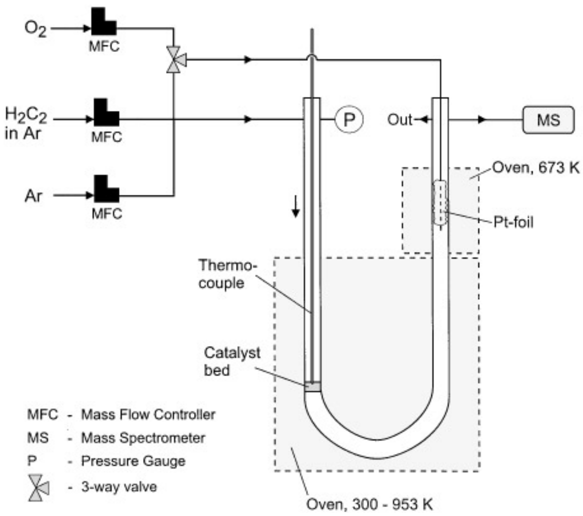

FIG. 1. The experimental apparatus used in the different temperature-programmed analyses.

METHODS

The Catalyst

Three different catalysts were used in the study (Table 1). A description of the preparation methods can be found in (14). The pellets originally prepared were crushed and sieved to avoid mass transfer limitations (14). The particle size was 0.3–0.4 mm.

Acetylene Hydrogenation

The deactivation experiments were performed in an internal recycle (Berty) reactor from Autoclave Engineers. Details about the apparatus can be found elsewhere (14). The deactivation was performed in a gas mixture of C_2H_4, C_2H_2, and H_2 with N_2 to balance. The total pressure was 1.0 MPa, the C_2H_4 partial pressure 0.3 MPa, and the temperature 313 K in all experiments. The partial pressures of C_2H_2 and H_2 for each experiment during the deactivation are given in Table 2. The duration of the deactivation was usually around 24 h (Table 2). The reaction rate was continuously measured during the deactivation. Directly after the prescribed deactivation time the gas composition was changed to the standard conditions (0.3 MPa C_2H_4, 3.5 kPa C_2H_2, and 7.0 kPa H_2 with N_2 to balance). The temperature and total pressure were kept unchanged. After 45 min under the standard conditions the ethane selectivity was recorded. Comparison of catalyst performance is thus made under equal conditions.

TABLE 1

Catalyst Properties

Catalyst	Carrier	Pd source	Pd load (wt%)	Dispersion (mol CO/ mol Pd)	Pore volume (cm^3/g)	BET surface (m^2/g)
A	α-Al_2O_3	$Pd(NO_3)_2$	0.05	0.035	0.23	8
B	α-Al_2O_3	$PdCl_2$	0.04	0.05	0.20	8

Determination of the Coke Concentration

Three different methods were applied in order to determine the coke concentration:

1. Measurement of the weight increase during a run. The reactor basket, including the catalyst, was weighed before and after the deactivation run on a standard laboratory balance. Prior to use, the catalyst was kept in a desiccator to avoid water contamination.
2. Measurement of the weight loss when the deposited coke was burned off in air at 1073 K. Reference samples of fresh catalyst were given the same treatment and the difference in weight loss was attributed to coke.
3. Temperature-programmed oxidation (see below).

Temperature-Programmed Oxidation

The experimental setup can be seen in Fig. 1. During the TPO experiments, oxygen (1 ml/min) and argon (24 ml/min) were used and the temperature in the main oven was increased from 300 to 953 K at a heating rate of 10 K/min. The temperature in the second oven was kept at 673 K during the whole experiment. A Pt foil catalyzed the oxidation of uncombusted hydrocarbons, and only CO_2 and H_2O were formed. The advantage of this technique, which was previously used by our research group (21), is that it is easy to estimate the amount of the desorbing hydrocarbons without knowing the often very complex composition.

TABLE 2

Experimental Plan with Reaction Conditions and Coke Concentrations

Run	Catalyst	$p_{C_2H_2}$ (kPa)	p_{H_2} (kPa)	$p_{C_2H_4}$ (kPa)	TOS[a] (h)	C_{w1}[b] (wt%)	C_{w2}[c] (wt%)	C_{TPO}[d] (wt%)	Ethane selectivity	Mean TOF[e](s^{-1})	Remark
1	A	7.0	0[f]	300	24	0.2			0.22		
2	A	3.5	7.0	300	25	2.26	2.44	2.50	0.16	1.20	TPO
3	A	7.0	7.0	300	24	3.75		3.71	0.16	0.83	TPO
3b	A	7.0	7.0	300	24	3.52		3.64	0.19	0.87	D_2 during deactivation[g]
4	A	7.0	2.8	300	29	1.20		1.36	0.55	0.34	TPO
5	A	7.0	36.0	300	20	3.40			0.23	4.27	
6	A	14.0	7.0	300	25	3.29			0.27	0.59	
7	A	3.5	11.7	300	24	3.00			0.20	1.98	
8	A	3.5	2.8	300	24	1.35			0.34	0.39	
9	A	7.0	17.2	300	31	1.21			0.45	0.44	90 ppm CO
10	A	7.0	17.0	300	24	1.88		1.62	0.41	0.56	50 ppm CO
11	B	7.0	7.0	300	24	3.40		3.51			TPO
12	B	7.0	7.0	300	48	5.68	5.72	5.59			TPO

Several TPO experiments were also performed on the catalyst deactivated in run 3:

			Time of exposure to air at room temperature before TPO or TPD (days)
13	See run 3	TPO with 3% O_2	48
14	See run 3	TPO with 6% O_2	49
15	See run 3	TPO with 8% O_2	50
16	See run 3	TPO without extra reactor	51
17	See run 3	TPD	27

Note. Constant conditions in all experiments: $T = 313$ K, $P_{tot} = 1.0$ MPa, N_2 to balance.

[a] Time on stream.

[b] Coke concentration, by the weight increase during the run.

[c] Coke concentration, by the weight loss by burning off the coke.

[d] Coke concentration, from TPO.

[e] The time average TOF during the deactivation. TOF is based on CO chemisorbtion measurement on fresh catalyst samples (Table 1).

[f] No H_2 in feed. Small amounts were detected during the first hours, presumably from C_2H_2 dissociation.

[g] The experiment was carried out with deuterium instead of hydrogen (22).

Temperature-programmed oxidation was also performed without the platinum foil in the second oven. This experiment was conducted in order to see how much coke in the first peak of the TPO spectrum consisted of hydrocarbons desorbing. The hydrocarbons were not analyzed.

A mass spectrometer (MS), Gaslab 300, Fisons Instruments, was used mainly to follow M/e 44 (CO_2), M/e 32 (O_2), and M/e 18 (H_2O). The presence of unburned hydrocarbons was checked for by using the MS. By burning different concentrations of acetylene, the CO_2, H_2O, and O_2 responses were calibrated. The hydrogen-to-carbon ratio in the coke was estimated from the CO_2 and H_2O formation.

After the coking experiment, the catalysts were placed in a container that was flushed with nitrogen, sealed, and put in a freezer. Immediately before the TPO experiments, the catalysts were taken out of the freezer and placed in the reactor, except for runs 13–17 (see Table 2).

The amounts of deactivated catalyst analyzed in the temperature-programmed studies were varied (43–140 mg) so that about the same amount of coke was burned in each experiment.

Temperature-Programmed Desorption

Temperature-programmed desorption of the coke accumulated on the catalysts was performed in the same apparatus described earlier. In these experiments, however, only argon (24 ml/min) was flowing through the catalyst bed. Oxygen (1 ml/min) was introduced after the bed, immediately before the Pt foil (see Fig. 1). The desorbing species reacted on the Pt foil and formed CO_2 and H_2O that were identified in the MS.

Deconvolution

The TPO peaks were deconvoluted using a kinetic model formulated by Querini and Fung (18),

$$\frac{dx_i}{dt} = A_i e^{-E_{Ai}/\mathrm{RT}} \cdot (1 - x_i)^{n_i} p_{O_2}^{m_i}, \qquad [1]$$

where x_i is the conversion of coke, A_i is a pre-exponential factor, E_{Ai} is the activation energy, n_i is the reaction order of coke, p_{O_2} is the partial pressure of oxygen, and m_i is the oxygen reaction order. A few different types of coke are usually assumed, and the index i denotes the type of coke.

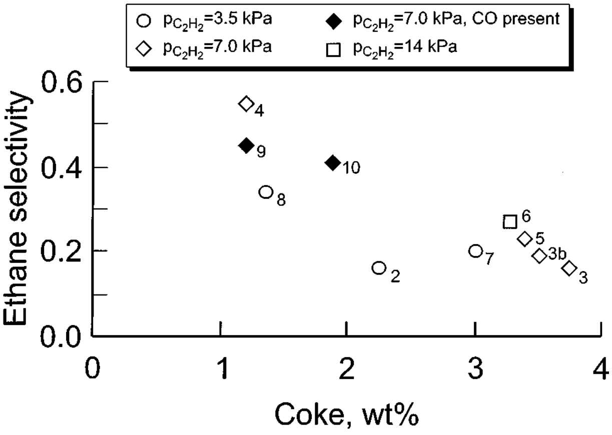

FIG. 2. Ethane selectivity under standard conditions (0.3 MPa C_2H_4, 3.5 kPa C_2H_2, and 7.0 kPa H_2 with N_2 to balance) obtained with catalyst samples coked at different reaction conditions. The numbers at each point correspond to run numbers in Table 2.

RESULTS

The Acetylene Hydrogenation

In all experiments, the decrease in acetylene hydrogenation rate during the deactivation was below 10% and the discussion will concern the selectivity and the coke only. The amounts of coke determined by three different methods can be found in Table 2. There is great consistency among the methods. The values achieved by direct weighing of the catalyst before and after the deactivation are more comprehensive, and will be used in the following analyses.

The ethane selectivity is plotted versus the coke content in Fig. 2. If the ethane selectivity had been directly related to the amount of coke, one would have expected a positive slope in the figure. However, this is not the case, which implies that the main fraction of the coke has a very limited influence on the catalyst properties aside from mass transfer effects (19). In the next section we concentrate on the characteristics of the coke by performing temperature-programmed oxidation on the deactivated samples.

Temperature-Programmed Oxidation

Results from the TPO experiments on catalysts aged under different reaction conditions are shown in Fig. 3. The most striking feature is that, for a given catalyst, the coke characteristics (peak shape and H/C ratio) are independent of gas composition. In contrast, the total amount of deposited coke varies substantially. However, the location of the TPO peaks is different on the two catalysts prepared by different precursors. On the $PdCl_2$ catalyst (cat. B) the peaks obtained at the highest temperature are shifted to lower temperature by about 40 K compared to the catalyst prepared by impregnation with $Pd(NO_3)_2$ (cat. A).

In order to study the coke located in the first peak in the TPO curves, a TPO experiment without the Pt foil in the second reactor and a TPD experiment were conducted. The former experiment showed that only small amounts of CO_2 are formed on the catalyst during the TPO experiment at temperatures lower than 530 K (curve iii in Fig. 4a). Pure desorption of hydrocarbons, without any influence by oxygen in the gas phase, cannot explain the whole first peak, because a higher oxygen pressure will result in a larger peak (compare curves i and ii in Fig. 4a and also Fig. 4b).

Before the TPD experiment; the TPO with 3, 6, and 8% O_2; and the TPO without Pt foil in the second reactor, the catalyst was exposed to air at room temperature for several weeks (Table 2). It is possible to see the effect of these different treatments on the first peak in the TPO profiles. The area of this peak is larger when the catalyst has not been exposed to air at room temperature for a longer time. The amount of coke measured by TPO also differs. With only a short exposure to air at room temperature 3.71 wt.% coke was detected (run 3, TPO with 4% O_2), while after 48

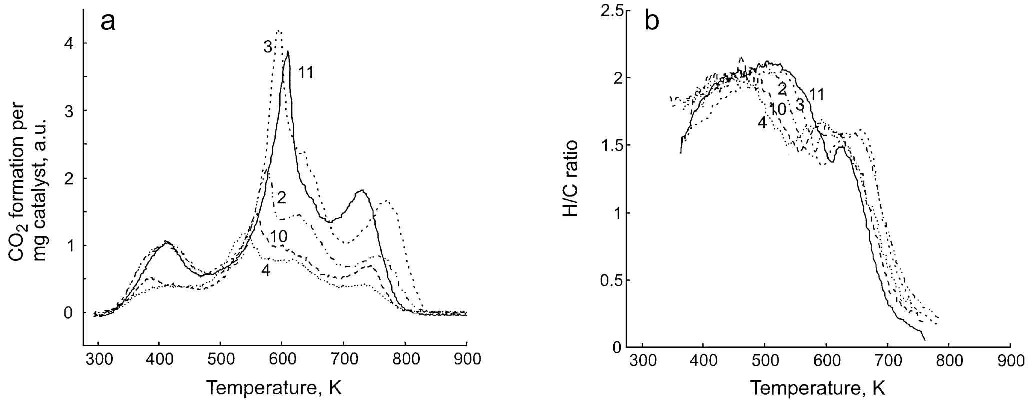

FIG. 3. TPO analyses of catalysts deactivated at different conditions (Table 2). The numbers at each curve correspond to run numbers in Table 2. The solid lines mark the catalyst similar to catalyst A, but impregnated with $PdCl_2$ instead of $Pd(NO_3)_2$ (cat. B). (a) The CO_2 formation and (b) the hydrogen-to-carbon ratio.

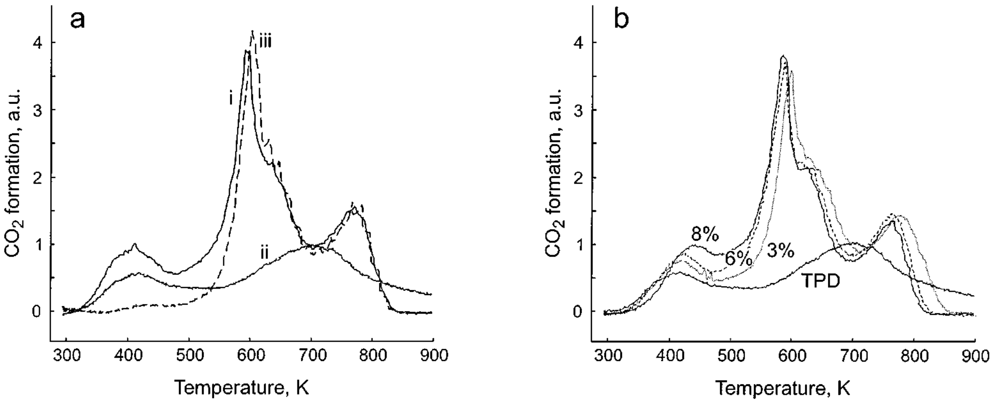

FIG. 4. (a) The CO$_2$ response at (i) normal TPO (run 3), (ii) TPD (run 17), and (iii) TPO without Pt foil in the second oven (run 16). (b) TPO profiles for experiments conducted at different partial pressures of oxygen and a TPD experiment. All experiments were carried out on a catalyst deactivated during the same experiment (run 3, Table 2).

days exposure to air at room temperature 3.55 wt.% coke was detected (run 13, TPO with 3% O$_2$).

Querini and Fung (18) obtained poor kinetic parameters when deconvoluting single TPO experiments. In order to improve the results, they regressed two independent sets of data, obtained at different heating rates. Because of this, we used Eq. [1] to deconvolute TPO profiles from experiments where the oxygen partial pressure was changed (Fig. 4b). The nature of the first peak in the TPO can be derived mainly from desorption, and the kinetic equation above is not suitable to use for deconvolution. Instead a Gaussian peak was estimated from the TPD experiment and this area was subtracted from the TPO profiles before performing the deconvolution (Fig. 5a). The deconvolution was then performed, and the results can be found in Fig. 5a and in Table 3. The parameters in Table 3 are determined for each peak *i*. The numbering is illustrated in Fig. 5b. It should be noted that $i = 1$ does not mean the desorption peak discussed earlier, but is mainly what is left after subtraction of the Gaussian curve, peak D.

The Effect of the Hydrogen Partial Pressure

The analysis continued by studying the influence of the partial pressure of hydrogen during the deactivation on the selectivity measured at standard conditions. From Fig. 6a the decisive role of the partial pressure of hydrogen is clear. However, the catalysts deactivated in the presence of carbon monoxide showed a high ethane selectivity once the carbon monoxide was removed. CO is known to hinder hydrogen adsorption and may thus decrease the hydrogen coverage on the metal surface. No direct information about the hydrogen coverage is available. Nevertheless, by

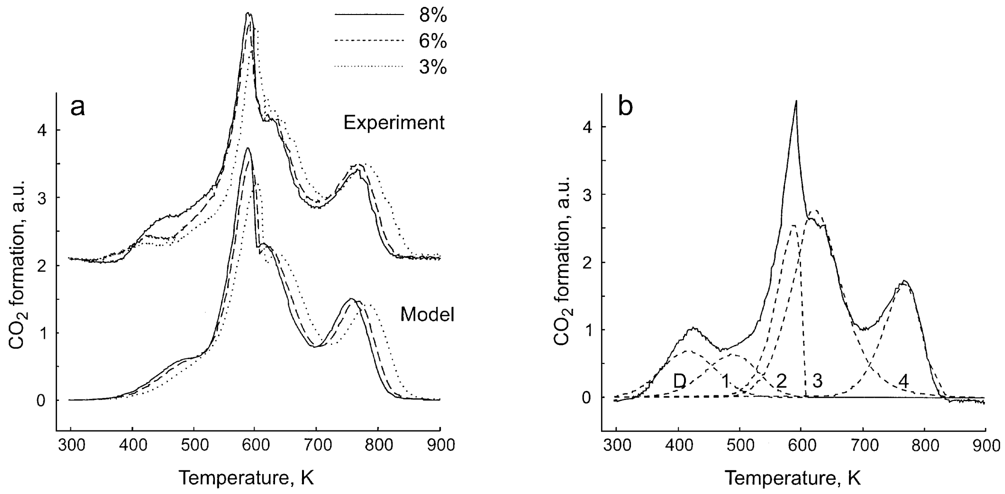

FIG. 5. (a) The experimental TPO profiles (runs 13, 14, and 15) after subtracting the contribution from the desorption, and results from the model. (b) Results from the deconvolution of the experiment conducted with an oxygen concentration of 6% (run 14, Table 2).

TABLE 3

Parameters Estimated from the TPO Experiments Conducted at Different Partial Pressures of Oxygen Using Eq. [1]

i	A_{is}	E_{Ai} (kJ/mol)	c_i (μmol)	n_i	m_i
1	$(3.06 \pm 0.43) \times 10^5$	47.75 ± 0.04	27.65 ± 1.38	1.120 ± 0.087	0.8108 ± 0.046
2	$(2.04 \pm 0.16) \times 10^{10}$	112.73 ± 4.04	51.13 ± 3.06	0.5568 ± 0.015	0.4936 ± 0.015
3	$(1.32 \pm 0.37) \times 10^{10}$	113.94 ± 9.56	119.13 ± 2.91	2.158 ± 0.198	0.7773 ± 0.061
4	$(7.72 \pm 1.01) \times 10^{12}$	177.64 ± 5.57	52.23 ± 1.30	1.214 ± 0.039	0.9581 ± 0.035

Note. Here i indicates the different peaks in the TPO spectra; 95% confidence intervals are given.

assuming that the acetylene hydrogenation rate is controlled by the surface reaction, the following equation can be formulated:

$$r = k\theta_{C_2H_2}\theta_{H_2}^{\beta}.$$

Except for very low concentrations of acetylene, the overall reaction order of acetylene is negative. The surface coverage of acetylene is close to unity, and one may assume that $\theta_{C_2H_2}$ is constant with little error. This means that the acetylene reaction rate is an explicit function of the hydrogen coverage θ_H. Figure 6b is based on this concept. It appears that the availability of surface hydrogen during deactivation has a crucial effect on the selectivity of a used catalyst.

The Effect of Hydrogen on the Coke Formation

The coke deposition after 24 h of operation is shown in Fig. 7a as a function of partial pressure of hydrogen. Contrary to previous findings (2, 10, 20), the coke concentration increases with the hydrogen pressure, at least at low values. The presence of CO reduces the coke deposition, presumably by reducing the surface coverage of hydrogen. In Fig. 7b the coke deposition has been plotted versus the rate of the acetylene formation, as discussed in the previous section. The coke formation is found to increase with the surface coverage of hydrogen.

DISCUSSION

The Effect of the Partial Pressure of Hydrogen on the Coke Formation

Figures 7a and 7b indicate that the coke formation rate increases with the surface coverage of hydrogen on the active metal. This is not in line with some earlier studies (2, 10, 20). However, the present study has been performed at relatively low partial pressures of hydrogen, and we may consider the possibility that the coke formation rate reaches a maximum and then decreases with increasing hydrogen pressure. It is also possible that we have already reached the maximum somewhere in the range 12–36 kPa hydrogen. In a previous study (21) we suggested that a half-hydrogenated surface intermediate (C_2H_3) is formed by hydrogenation of acetylene. This intermediate can either form ethene (22, 23) or, if the hydrogen coverage is low, react with other species on the surface and form coke or coke precursors (21). This mechanism would explain the complex effect of the hydrogen partial pressure on the coke deposition rate.

The Effect of Coke on the Selectivity

From this study it is also clear that the total amount of coke is of minor interest for the changes in selectivity during acetylene hydrogenation. At first glance, this stands in contradiction to what is previously found. However, in most

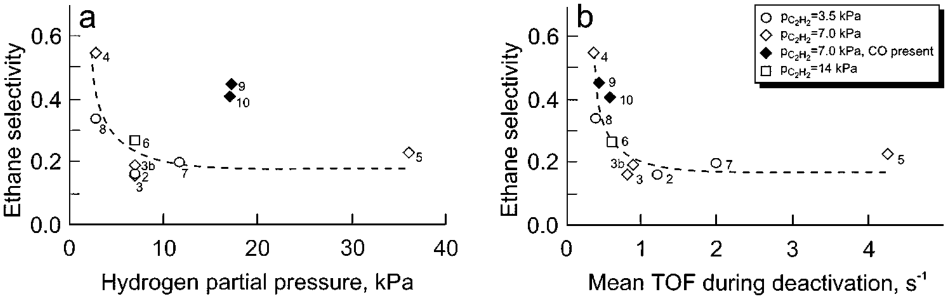

FIG. 6. (a) The influence of hydrogen partial pressure during deactivation on ethane selectivity under standard conditions. (b) Ethane selectivity under standard conditions versus mean reaction rate for acetylene consumption during deactivation. This rate is assumed to be proportional to the surface coverage of hydrogen. The numbers at each point correspond to run numbers in Table 2.

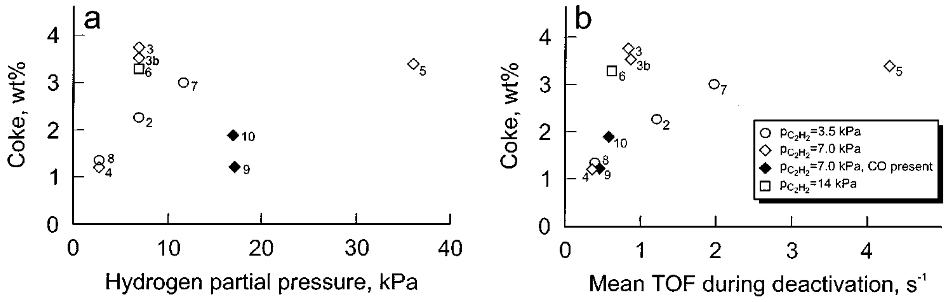

FIG. 7. (a) The influence of the partial pressure of hydrogen during deactivation on coke concentration. (b) The coke concentration versus mean reaction rate for acetylene consumption during deactivation. This rate is assumed to be proportional to the surface coverage of hydrogen. The numbers at each point correspond to run numbers in Table 2.

earlier studies the selectivity changes and the coke formation rate have been measured simultaneously as a function of time. The same results would have been the outcome also in the present study using the same approach. Instead we let the catalyst deactivate under different conditions for a given time period. After that the selectivity toward ethane formation was estimated under the same reaction condition in all experiments. It turns out that the surface coverage of hydrogen during the deactivation is of great importance in reducing the formation of the coke responsible for the increased selectivity to ethane formation.

Sárkány *et al.* (3) discussed a mechanism whereby ethene is adsorbed and hydrogenated to a large extent on the support or the coke surface. Spillover hydrogen is required in the latter reaction, and the role of coke is primarily to promote hydrogen transfer from the metal surface to the adsorbed ethene. Sermon *et al.* (24) used a special combined fixed-fluidized bed reactor. They have shown that coke deposited on a silica–alumina catalyst is catalytically active in the hydrogenation of cyclohexene at 343 K if dissociated hydrogen is available by spillover. They also concluded that polyaromatic compounds were responsible for the catalytic activity.

In the previous section about the effect of the partial pressure of hydrogen on the coke formation, a mechanism was proposed. We can extend this mechanism to also explain the role of hydrogen in altering the selectivity. The half-hydrogenated surface intermediate (C_2H_3) could at low hydrogen availability form a coke precursor (C_4H_6). We now suggest that this coke precursor could form two types of coke, one harmful type that causes unwanted formation of ethane by, for example, a spillover mechanism as previously discussed (3, 24), and one harmless type. The two types of coke are formed in parallel and the great majority of the coke is harmless. A similar mechanism was proposed by Larsson *et al.* (19) for propane dehydrogenation. Figure 8 shows one possible mechanism. The harmless coke is here formed by a reaction with hydrogen. At very low surface coverage of hydrogen, coke of the harmful type would be formed almost exclusively. When the hydrogen available on the catalyst increases, the total amount of coke formed also increases, but mainly the harmless type. At even higher hydrogen coverage, coke formation is suppressed. The suggested mechanism showed in Fig. 8 is not the only one possible. Other mechanisms with a higher hydrogen reaction order for the formation of harmless coke than for the formation of harmful coke could also explain the observed effect of hydrogen on the selectivity.

Coke

We found that the different reaction conditions resulted in no significant differences in the TPO profiles other than the amount of coke, although the shape of the profile differs between the catalysts impregnated with $PdCl_2$ and $Pd(NO_3)_2$. This implies that the composition and location of the coke are independent of reaction conditions. We may conclude that the key to how the different gas compositions cause different deactivation cannot be found from the TPO experiments.

The slightly different shape of the TPO profile for the catalyst impregnated with $PdCl_2$ can be explained by the presence of Cl^- ions in this catalyst. This might influence the type or location of the coke formed, thus leading to the peaks in the TPO spectra from the Cl^- containing catalyst shifts compared to the catalyst without Cl^-. Augustine *et al.* (34) report that the presence of Cl^- on Pt/Al_2O_3 affects the mobility of the coke so that more coke is retained on the support. Although our catalyst is quite different we may speculate that the same phenomenon may occur on our catalyst. It is also possible that the presence of Cl^- affects the activation energy for the coke burn-off, thus leading to different peak temperatures.

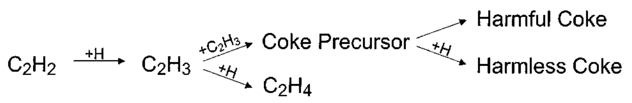

FIG. 8. A possible coke formation mechanism explaining the influence of the surface coverage of hydrogen on the formation of harmful and harmless types of coke.

From Fig. 4a, it is possible to infer that the coke in the major part of the first peak in the TPO spectrum consists of heavy hydrocarbons that are adsorbed on the catalyst surface or absorbed in the pore system. This is also consistent with the decrease of this peak upon long exposures to air at room temperature previously discussed. However, oxygen assists the desorption (Fig. 4b). Explanations could be that oxygen cleans the metal surface from adsorbed hydrocarbons, or that the oxygen reacts with heavy hydrocarbons, causing a cleavage and formation of lighter hydrocarbons that desorb.

We can draw conclusions about the type of coke found on the catalyst by studying the parameters determined through the deconvolution (Table 3). The peak $i = 1$ is difficult to evaluate because of the proximity of the desorption peak. For the next two peaks, $i = 2$ and $i = 3$, the activation energies, 113 and 114 kJ/mol, are well in the range found by others for coke on supported metal catalysts (25). The most important difference between the two peaks is the reaction order of coke, $n = 0.56$ and $n = 2.2$ for $i = 2$ and $i = 3$, respectively. As has been discussed in detail by Querini and Fung (18) and Butt and Petersen (26), the coke reaction order depends upon the geometry and how coke is consumed during the oxidation process. If all carbon atoms are exposed, then $n = 1$. Spherical coke particles will result in $n = 2/3$, and if the number of exposed carbon atoms is unchanged during combustion, as could be the case if multiple layers of coke exist, then $n = 0$. A reaction order of coke of 0.56 as for $i = 2$ is a reasonable value if all carbon atoms are not exposed, as will be the case if larger coke particles are formed or if pores are plugged. The value $n = 2.2$ is not reasonable if only one type of coke is assumed. However, Cider and Schöön (27) have shown that a number of first-order reactions, having an exponential rate-constant distribution, will give an apparent second-order reaction. Using the same motivation, we propose that the peak $i = 3$ consists of a distribution of different coke types. Furthermore, another explanation may be that the coke, while heated during the TPO, changes structure, thus generating a different type of coke. This is not unlikely to happen since the temperature where peak $i = 3$ occurs is about 300 K higher than the reaction temperature.

The oxygen reaction order has also been determined individually for the different types of coke (Table 3). For the peak $i = 2$ it is very close to 0.5, which would be the reaction order if the rate-determining step were the reaction between coke and a single dissociated oxygen atom (28). An oxygen reaction order of one, on the other hand, can be found either if a noncatalytic direct oxidation of the coke occurs or if, in the catalytic reaction discussed above, the adsorption of oxygen is the rate-limiting step. Other possible catalytic mechanisms resulting in an oxygen reaction order of one may occur if two dissociated oxygen atoms react with the coke or if CO oxidation is the rate-limiting step. For the next peak ($i = 3$) $m = 0.78$. This value is reasonable if a combination of the above reactions takes place. These estimations of the oxygen reaction order are in good agreement with results by Pieck *et al.* (29), who estimated it to be 0.5 in burning coke on a commercially coked Pt–Re/Al_2O_3 naphtha-reforming catalyst. Liu *et al.* (28) found that the reaction order in oxygen partial pressure was 0.55 for a Pt–Sn reforming catalyst and 0.75 for zeolite cracking catalyst.

For the last peak ($i = 4$) the activation energy is much higher, 178 kJ/mol. This value corresponds well to the burning of graphite (35) and indicates a more graphite-like type of coke. The coke reaction order is 1.2, which is reasonable for a type of coke where all carbon atoms are exposed, i.e., the coke is well dispersed on the support. Furthermore, another possibility is, of course, that a distribution of different coke types exists or that the structure of the coke changes during the heating. The oxygen reaction order is close to one and the coke combustion probably takes place through direct oxidation of the coke by oxygen in the gas phase.

We agree with a model, earlier proposed by others (28, 30–32), that a small part of the coke is located on the metal, while a larger part is placed close to the metal and is assisted by the metal in the combustion. The coke identified in peaks $i = 2$ and 3 is coke on and in the vicinity of the palladium, and the peak $i = 4$ indicates coke deposited on the carrier combusted without any influence by the metal.

We previously performed experiments using deuterium as a tracer during the acetylene hydrogenation (21). From these results a mechanism for the coke formation was proposed. We also found that the ratio between deuterium and hydrogen in the coke formed on the catalyst was constant for all types of coke, when studied during a TPO experiment, and we can conclude that the same mechanism is valid for formation of all types of coke.

The Methods

The treatment of the coked catalyst before the TPO experiment is important in order to give reproducible results. Long exposure to air after the coking experiment was found to reduce the first peak. It is recommended that catalyst be kept in the freezer and exposure to air minimized after coking.

From Table 2 it can be seen that the amounts of coke obtained by TPO and weighing agree very well for the Pd/α-Al_2O_3 catalysts. However, if, for example, γ-Al_2O_3 is used as support, problems arise with water adsorbed on the carrier, and the agreement would be less consistent. Asplund (14) reports that a fresh γ-Al_2O_3 catalyst lost about 5% of its weight when oxidized at 1073 K whereas an α-Al_2O_3-supported sample lost no weight at all. As discussed earlier, the treatment between the coking reaction and the TPO experiment is crucial, and it is desirable to conduct the TPO experiment directly after the coking in the same apparatus.

The design of the TPO reactor had some important features that proved to work very well in the experiments. First, the extra reactor with the heated Pt foil was necessary to be able to detect the amount of coke in the desorption peak. Another approach would be to try to determine the composition directly, either in the gas phase during the TPO (33) or by extracting the soluble parts of the coke (11). In both cases a GC-MS analysis is desirable because of the very complex composition. In this work we have tried to determine only the quantity and the H/C ratio, which can be difficult by the methods discussed above. A further feature of the experimental equipment was the possibility to add oxygen after the catalyst bed and burn everything that desorbs during the TPD experiment. The experiment was fast to perform and evaluate, and gave accurate results.

CONCLUSIONS

We found that the total amount of coke was of minor importance in explaining the undesired increased selectivity to ethane formation. Neither did the TPO analyses reveal any evidence that the characteristics of the coke are important for ethane selectivity. Instead, the surface coverage of hydrogen has a crucial role in the selectivity phenomenon. A low surface coverage leads to a larger increase in ethane selectivity than does a higher surface coverage of hydrogen. More “harmful” coke is formed, but this coke cannot be identified in the TPO analyses. The coke formation rate is also increased when more hydrogen is present on the surface, at least at relatively low hydrogen pressures. The role of carbon monoxide is to reduce the surface coverage of hydrogen, leading to higher ethane selectivity and diminished coke formation.

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