

Chemical State and Reactivity of Supported Palladium

II. Support Effect and Catalyst Activation by the Reaction Mixture in Ethylene Oxidation

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The oxidation of ethylene over supported palladium was studied in a steady-state flow microreactor, taking into account the influence of various experimental factors such as the nature of the carrier (aluminas, silica, titania), the kind of precursor (chloride, nitrate, amine), the preparation mode, the metal loading, and the nature of pretreatments. It is first confirmed that, at low conversion, significant selectivities to acetic acid (AcOH) may be obtained. Clear evidence is presented for a dual state behavior of the catalysts. For freshly reduced samples the activity for total oxidation and the AcOH selectivity are low for the majority of samples below 383°K and seem to depend upon palladium-carrier interactions. However, after working at high conversion with oxygen-rich mixtures, the activity and the selectivity are enhanced and become identical for all catalysts. The origin of this activation phenomenon by the reaction mixture is discussed; it is proposed that working at high conversion leads to the destruction of palladium-carrier interactions and induces a surface reconstruction.

INTRODUCTION

In a previous paper (1), we presented an investigation of the chemical state and environment of supported palladium. The nature of the surface complexes produced upon impregnation and drying was shown to depend on the nature of carrier; the influence of the support on the chemical state of palladium after reduction was also observed and attention was drawn to the presence of residual chlorine on the catalyst surface.

The present work deals with activity patterns in the oxidation of ethylene. From earlier investigations, palladium appeared to yield only total oxidation products (2-4); however, in some cases small amounts of acetic acid were observed (5, 6)

and recently significant selectivities to acetic acid were obtained at low conversion on Pd sponge and Pd/SiO₂ (7). The aim of the present paper is to try to correlate activity and selectivity data with the factors affecting the catalyst elaboration such as (i) the preparation technique (ion exchange or impregnation), (ii) the nature of the precursor solution, (iii) the nature of the carrier (aluminas, silica, titania), (iv) the metal loading, and (v) the nature of the pretreatments.

EXPERIMENTAL METHODS

The catalysts were prepared as previously described (1, 8). Some of their characteristics are presented in Table 1. All the kinetic data reported here were

TABLE 1
 Characterization of Pd Catalysts

Catalyst	Precursor	Metallic surface area ^a (m ² /g metal)	Percentage dispersion ^b	Average particle diameter ^c (nm)
Impregnation technique				
1.4% Pd/TiO ₂	PdCl ₂	57	10	9
10% Pd/TiO ₂	PdCl ₂	39	7	13
10% Pd/SiO ₂	PdCl ₂	39	7	13
10% Pd/SiO ₂	Pd(NH ₃) ₄ Cl ₂	42	7.5	12
10% Pd/SiO ₂	Pd(NO ₃) ₂	40	7	12.5
5% Pd/ δ -Al ₂ O ₃	Pd(NH ₃) ₄ Cl ₂	42	7.5	12
5% Pd/ δ -Al ₂ O ₃	PdCl ₂	41	7.5	12
5% Pd/ δ -Al ₂ O ₃	Pd(NO ₃) ₂	78	14	6.5
10% Pd/ δ -Al ₂ O ₃	PdCl ₂	42	7-8	11-13
10% Pd/ δ -Al ₂ O ₃ , H ₂ O pretr.	PdCl ₂	40	7	12.5
10% Pd/ η -Al ₂ O ₃	Pd(NO ₃) ₂	145	26	3.5
10% Pd/ η -Al ₂ O ₃	Pd(NH ₃) ₄ Cl ₂	33	6	15.5
10% Pd/ δ -Al ₂ O ₃ , H ₂ O pretr.	Pd(NO ₃) ₂	150	26	3.5
1.25% Pd/ δ -Al ₂ O ₃	PdCl ₂	51	9	10
Cationic exchange method				
4% Pd/SiO ₂	Pd(NH ₃) ₄ Cl ₂			2-3 ^d
4% Pd/SiO ₂ after reaction	Pd(NH ₃) ₄ Cl ₂	72	13	7 ^d
4% Pd/SiO ₂ calcined and reduced	Pd(NH ₃) ₄ Cl ₂	53	9.5	9.5 ^d

^a From CO uptake, taking 7.6 Å² for a palladium atom area (θ), or from $S = 6/\rho d$.

^b From CO uptake (assuming a 1/1 CO/Pd ratio) or from dispersion = 0.9/ d .

^c From X-ray line-broadening, or CO uptake.

^d From electron microscopy.

obtained at 1 atm total pressure in a steady-state flow microreactor. The measurements were generally performed at low conversion (usually $\leq 5\%$). Even in those conditions the reactor temperature had to be carefully controlled because of the high exothermicity of the reaction (1386 kJ mol⁻¹ for the total oxidation of ethylene). In order to determine the temperature limit of the kinetically controlled steady-state reaction, the ignition point of the system had to be estimated. For the Pd/Al₂O₃ samples, this point was attained for a reactor temperature of about 503°K. For Pd/SiO₂ and Pd/TiO₂, this temperature was around 403°K only. Working with a palladium wire Schwartz and co-workers (10) reported ignition temperatures of 514

and 559°K for reaction mixtures containing 2% ethylene plus 40 and 10% oxygen, respectively.

In our experimental conditions, the reaction became uncontrolled when the apparent temperature of the catalytic bed was around 10°K above that of the vessel. Moreover, working beyond the ignition limit results in a strong modification of the catalytic properties. Consequently, two experimental procedures are imposed by the ignition temperature values: (i) In the temperature range where the reaction is kinetically controlled, the apparent increase of the catalyst temperature is only 3 to 5°K above that of the vessel (e.g., 473°K for Pd/Al₂O₃); the kinetic measurements performed in this case on a *freshly*

reduced sample are referred to as *first state activity*. (ii) In the second procedure, the catalyst was left for several hours in "explosive" conditions; then the reactor was cooled down to room temperature and the *second state activity* was measured at various temperatures, the apparent increase of the catalyst temperature being restricted as above. Activities and selectivities were calculated according to the definitions already reported (7, 8).

RESULTS AND DISCUSSION

I. Evidence for a Dual State Activity

Figure 1 shows the results obtained with a 10% Pd/Al₂O₃ catalyst. The first state activity is low but, after working in "explosive" conditions, a significant increase in activity and selectivity is observed (second state). This activation is especially important for Pd/Al₂O₃, medium in the case of Pd/TiO₂, and absent for Pd/SiO₂. A similar activation was found for the vinylcyclohexane oxidation over Pd/Al₂O₃ (11). From a general point of view, it was rather difficult to obtain reproducible data with freshly reduced catalysts, i.e., in their first state, but the reproducibility was fairly good for the second state experiments.

1. Evidence for a support effect in the first activity state. In a preliminary approach, we report the *minimal detection temperatures*, i.e., the temperatures required

TABLE 2
Minimal Detection Temperatures for Catalysts Prepared by Impregnation ex PdCl₂^a

Catalyst	Metal surface area (m ² /g metal)	CO ₂ θ ₁ (°K)	AcOH θ ₂ (°K)
10% Pd/SiO ₂	39	358	363
10% Pd/TiO ₂	39	373	408
10% Pd/Al ₂ O ₃	41	393	463

^a Catalyst charge, 300 mg; p_{O₂}⁰ = 72 Torr; p_{Et}⁰ = 42 Torr.

TABLE 3
Activity and Selectivity^a of Freshly Reduced Catalysts (10% Pd)

Catalyst	Temperature (°K)	Percent-age conversion	Acid selectivity
Pd/δ-Al ₂ O ₃	373	0	
	423	0-1	
	473	5	10-15
	503	55-60 ^b	0-1 ^c
Pd/SiO ₂	368-373	5-10	25-30
	423	60-65 ^b	0-1 ^c
Pd/TiO ₂	373	Traces	—
	423	10-15	15-20
	443	55-60 ^b	5 ^c

^a Initial feed stream composition: p_{Et}⁰ = 42 Torr; p_{O₂}⁰ = 72 Torr; catalyst weight, 300 mg.

^b Uncontrolled temperature conditions.

^c Temperature at which the catalytic decomposition of AcOH occurs.

for detecting 0.1 Torr of product in the outgas stream in standard conditions. Table 2 shows the data obtained for samples containing 10% Pd. The decreasing activity order is: Pd/SiO₂ > Pd/TiO₂ > Pd/δ-Al₂O₃. The same classification appears

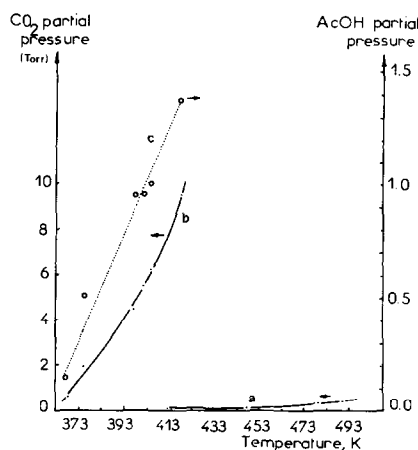


FIG. 1. Evidence for a dual state activity. Catalyst 10% Pd/δ-Al₂O₃ (ex PdCl₂). p_{O₂}⁰ = 72 Torr; p_{Et}⁰ = 15 Torr; catalyst charge, 100 mg; flow rate, 1.1 liter hr⁻¹. (a) CO₂ production, first state of activity; (b) CO₂ production, second state of activity; (c) AcOH production, second state of activity.

TABLE 4
Selectivity to Acetic Acid at 5% Ethylene Conversion for Freshly Reduced Catalysts^a

Catalyst	Temperature (°K)	AcOH selectivity
10% Pd/SiO ₂	378	15
10% Pd/TiO ₂	388	15
10% Pd/ δ -Al ₂ O ₃	503	8-10

^a Initial feed stream, $p_{Et}^0 = 12$ Torr; $p_{O_2}^0 = 72$ Torr; catalyst weight, 100 mg.

in Tables 3 and 4 where activity and selectivity data are compared. The 10% Pd/SiO₂ sample is much more active than 10% Pd/TiO₂ and 10% Pd/ δ -Al₂O₃. The latter catalyst exhibits no significant activity below 473°K, but every time a new reaction temperature is attained, a small amount of acetaldehyde is formed, which rapidly disappears. Acetic acid (AcOH) is detected only at 463°K. It is relevant to note that AcOH is catalytically decomposed over this sample at 473°K, which could explain the drastic decrease of selectivity between 473 and 503°K (Table 3).

2. *Disappearance of the carrier effect in the second state.* In contrast, the second state activity (expressed in turnover numbers) is nearly the same for all the 10% Pd samples (Fig. 2). In addition, when the Pd content is lowered to 1-2%, the turnover numbers differ by less than an order of magnitude (Fig. 3). The catalytic activity

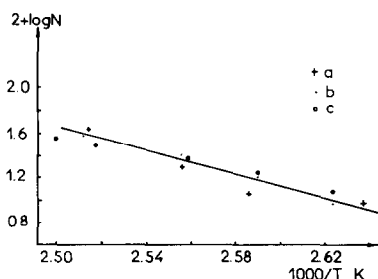


FIG. 2. Second state of activity: turnover number (min^{-1}) variation versus $1/T$. Metal loading, 10%; $p_{O_2}^0 = 75$ Torr; $p_{Et}^0 = 15$ Torr, (a) Pd/TiO₂; (b) Pd/ δ -Al₂O₃; (c) Pd/SiO₂.

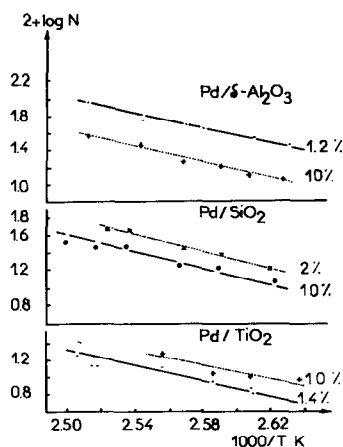


FIG. 3. Second state of activity. Influence of metal loading upon turnover number (min^{-1}) (initial oxygen pressure/initial ethylene pressure = 5).

is significant at a temperature as low as 373°K and the selectivity in AcOH attains 35 to 45%. Table 5 summarizes these findings in the case of Pd/TiO₂ for two different metal contents (it must be taken into account that the 1.4% Pd sample contain four times less exposed atoms).

3. *Influence of the partial pressures of the reactants.* According to the first state measurements, the reaction rate decreases when the initial ethylene pressure in-

TABLE 5
Conversion and Selectivity in the Second State for Pd/TiO₂^a

Catalyst	Temperature (°K)	Ethylene percentage conversion	AcOH selectivity
10% Pd/TiO ₂ ^b	353-373	2	45-35
	373-393	2-10	35-10
	393-408	10-20 ^c	10-5 ^c
1.4% Pd/TiO ₂ ^d	383	2	30
	383-393	2-5	30-20
	393-403	5-8	20-15
	403-423	8	20-10

^a $p_{O_2}^0 = 72$ Torr; $p_{Et}^0 = 42$ Torr.

^b Catalyst weight; 300 mg \rightarrow 30 mg Pd.

^c Uncontrolled temperature conditions.

^d Catalyst weight in order to have 5 mg Pd.

creases. Tables 6 and 7 show the results obtained with oxygen-rich reaction mixtures on 10% Pd and 1.4% Pd catalysts. Table 7 indicates also that the oxygen order is positive. On the other hand, in the second state of activity, a much smaller inhibition effect of ethylene is observed. It is also important to note that the catalyst activation (i.e., the obtaining of the second state) is effective only when oxygen-rich mixtures are used (Fig. 4).

4. *Selectivity in acetic acid.* In the first activity state, the selectivities measured over Pd/SiO₂ and Pd/TiO₂ are nearly equal but much smaller values are obtained with Pd/Al₂O₃ samples (1.25 and 10% Pd). This result can be accounted for by several assumptions. First, the sites on Pd/Al₂O₃ are less active and acetic acid is formed in the temperature range where this decomposition into CO₂ and H₂O begins to occur. Second, acetic acid begins to be produced near 370°K but, as it is strongly adsorbed as suggested by infrared data (12), it cannot be evolved without decomposition. On the other hand, the selectivity data obtained for the second state are of the same order of magnitude whatever the support, the preparation mode, the pretreatment procedure, and the metal content. These results mean that, going from the first to the second state, the catalyst surface has become uniform,

TABLE 6

Influence of Ethylene Pressure on Reaction Rate in the First Activity State for 10% Pd/TiO₂^a

p_{Et}^0	Rate: CO ₂ (mol sec ⁻¹ g ⁻¹ × 10 ⁻⁸)
11	20
15	19
30	7
40	3
44	1.3

^a Catalyst charge, 350 mg; $p_{O_2}^0 = 72$ Torr; temperature, 388°K.

TABLE 7

Partial Pressure Effect on Conversion in the First Activity State^a

$p_{O_2}^0$	p_{Et}^0	Percentage conversion
75	40	1.75
12	40	0.6
75	10	3.5

^a Catalyst, 1.4% Pd/TiO₂; temperature, 455°K; catalyst charge, 350 mg.

that is, equivalent sites exist on all samples. However, significant selectivity values can be obtained only when working at low conversion.

5. *Apparent activation energy.* As pointed out before, the reproducibility of experimental data was rather bad on freshly reduced Pd/Al₂O₃ and Pd/TiO₂ samples and it was very difficult to extrapolate an activation energy value. In contrast, the 2 and 10% Pd/SiO₂ catalysts gave good fittings for Arrhenius plots in the initial stage of the reaction (Fig. 5), the activation energy being about 70 kJ mol⁻¹ (partial oxidation) and 80 kJ mol⁻¹ (total oxidation) (8), in good agreement with the findings of Cant and Hall for 5% Pd/SiO₂.

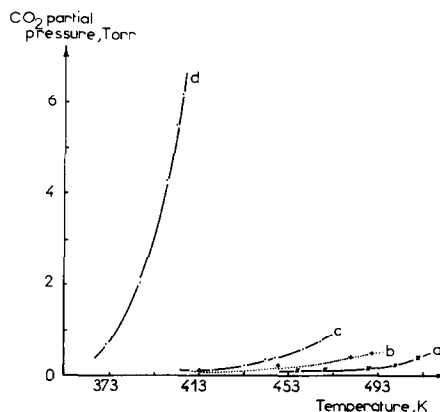


FIG. 4. Influence of the oxygen/ethylene ratio (O/E) on the second state activity. Catalyst, 10% Pd/ δ -Al₂O₃ (ex PdCl₂); catalyst charge, 100 mg; flow rate, 1.0 liter hr⁻¹. (a) First state, O/E = 1/4; (b) first state, O/E = 5/1; (c) second state, O/E = 1/4; (d) second state, O/E = 5/1.

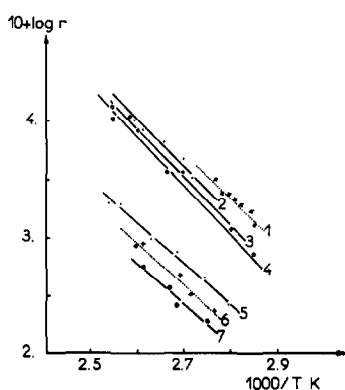


FIG. 5. Apparent activation energies for total or partial ethylene oxidation (r is expressed in mol sec⁻¹ g⁻¹). Metal loading, 10%; initial pressures, $p_{O_2}^0 = 72$ Torr; $p_{E}^0 = 12$ Torr. (a) Total oxidation: (1) Pd/SiO₂, first state; (2, 3, 4) second state for Pd/Al₂O₃, Pd/SiO₂, and Pd/TiO₂, respectively; (b) partial oxidation, second state: (5) Pd/Al₂O₃; (6) Pd/SiO₂; (7) Pd/TiO₂.

Such an agreement is not unexpected when considering that, for silica-supported catalysts, the second state activities (CO₂ or AcOH productions) do not differ from the first state ones (Fig. 5). Furthermore, the activation energies measured in the second state do not depend upon the nature of the carrier (alumina, titania, silica).

6. *Influence of the nature of the precursor* (Table 8). Some Pd/SiO₂ and Pd/ δ -Al₂O₃ samples were prepared by impregnation from Pd(NO₃)₂ and Pd(NH₃)₄Cl₂ solutions and reduced under H₂ at 573°K for 6 hr. The results obtained were quite similar to those reported above with catalysts prepared from PdCl₂: The Pd/SiO₂ catalysts are much more active and selective than the Pd/Al₂O₃ samples, whatever the nature of the precursor. In addition, after working at high conversion, all samples have the same activity.

7. *Influence of the preparation method*. The preceding kinetic data pertained to samples prepared by the impregnation method. Another series of catalysts was obtained by cation-exchange from Pd-(NH₃)₄Cl₂ aqueous solutions and reduction under flowing hydrogen at 373°K for

2 hr. In the case of Pd/ δ -Al₂O₃ (2% Pd), no activity was detected up to 493°K but the second state activity was similar to that observed with other alumina-supported samples. In contrast with the corresponding impregnated samples, the freshly reduced Pd/SiO₂ catalysts (2 and 4% Pd) showed no activity below 473°K; however, these samples were able to reach a second state activity as described above and the Pd particle diameter was simultaneously increased from 2 to 3 to 7 nm. The influence of the particle diameter being suspected, fresh Pd/SiO₂ (ion exchange) samples were calcined at 673°K and reduced by hydrogen at 573°K before the run. Whereas the mean particle size rises to about 9.5 nm, the minimal detection temperature (0.1 Torr of CO₂) decreases to about 443°K. For the impregnated Pd/SiO₂ sample presenting similar particle size and metal loading, the minimal detection temperature was about 363°K. Thus, in the case of Pd/SiO₂, the first state activity appears to depend upon the preparation mode, the use of the cationic exchange method resulting in a decrease of activity. However, in that particular case, a parallel increase of activity and metal particle size is noted. Then the exaltation of activity induced by working at high conversion (uncontrolled temperature conditions) appears to be a general feature of the present study. The origin of this exaltation and of the resultant uniformity of the catalytic properties now has to be questioned.

II. Attempts to Simulate the Activating Effect of the Reaction Mixture Working at High Conversion

This section deals with the influence of pretreatments by a reactant or a product upon the catalytic behavior. Pretreating freshly reduced catalysts with oxygen in the 523–653°K range (760 Torr, 14 hr), has no effect in the case of Pd/Al₂O₃ and leads to a deactivation for Pd/TiO₂ and

Pd/SiO₂. For 10% Pd/SiO₂ the minimum detection temperature is about 423°K (about 363°K for the untreated sample). The chemical state of Pd on these oxidized samples must now be elucidated. According to chemisorption data, the action of oxygen below 573°K may generate a nonstoichiometric phase (13) or lead to bulk oxidation (14). On the other hand, X-ray diffraction studies by Guiot (15) suggest that, in the 453–573°K range, a “three-dimensional surface complex” different from PdO is formed. More recently, Lam and Boudart (16) have observed some diffraction lines of PdO on silica-supported palladium exposed to oxygen at 543°K. After heating in oxygen at 653°K, our catalysts were examined by X-ray diffraction and uv visible spectroscopy. Whereas no definite oxide phase was detected by X-rays, the presence of PdO can be inferred from the reflectance spectra. In all cases, indeed, a band is recorded in the 430–480 nm range (the color being brown) whereas unsupported PdO shows a peak near 435 nm (17) and Pd metal no band at all in this interval.

Another series of experiments was carried out to try to activate the preoxidized Pd/SiO₂ and Pd/Al₂O₃ samples by an oxygen-rich reaction mixture. After working near 473°K and cooling, both catalysts began to be active below 373°K and their color became dark. In addition, the uv visible spectra show a drastic intensity decrease of the band near 450 nm. It may therefore be inferred that working at high conversion leads to the (partial at least) reduction of the preoxidized catalyst.

The influence of pretreatments with ethylene, carbon dioxide, or water was also examined. While exposure to ethylene induces a decrease of activity, a pretreatment in CO₂ causes a slight activity enhancement. But the most interesting feature concerns the influence of water vapor. Its activating effect for 5% Pd/Al₂O₃ is clearly shown in Fig. 6: For total oxida-

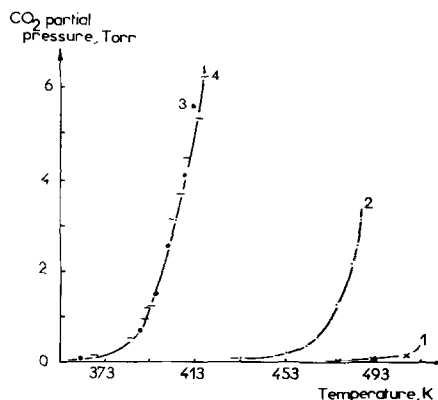


FIG. 6. Effect of a pretreatment by water vapor (24 hr at 523°K, 20 Torr). Catalyst, 5% Pd/Al₂O₃ ex Pd(NO₃)₂; charge, 100 mg; flow rate, 1.0 liter hr⁻¹; $p_{O_2}^0 = 72$ Torr; $p_{Et}^0 = 25$ Torr. (1) Untreated, first state; (2) pretreated, first state; (3) untreated, second state; (4) pretreated, second state.

tion the minimum detection temperature falls to 353°K (423°K for AcOH production). However, Fig. 6 demonstrates that this activation procedure is less efficient than that involving the catalyst working at high conversion. This is true even though long times (24 to 40 hr) and rather high temperatures (523 to 623°K) of pretreatment are employed. In addition, all the catalysts pretreated by water vapor are further activated by the reaction mixture in highly exothermic conditions, their activity becoming identical to the second state of activity of nonpretreated samples.

In conclusion, it appears that the activation phenomena cannot be accounted for by an interaction between one reactant alone and the catalyst. Water vapor seems to play a role but it cannot be considered as the unique factor responsible for the activating process.

III. The Origin of the Second State Activity

From the preceding data, evidence is given that, except for impregnated palladium-silica samples, the catalysts are activated by working at high conversion,

TABLE 8
Minimal Detection Temperatures and Selectivity for Catalysts Prepared by
Impregnation from Precursors Other than PdCl₂

Catalysts	Precursors	CO ₂ θ ₁ (°K)	AcOH θ ₂ (°K)	Mean AcOH selectivity at θ ₂
10% Pd/η-Al ₂ O ₃	Pd(NO ₃) ₂	443	478-483	10-20
10% Pd/η-Al ₂ O ₃	Pd(NH ₃) ₄ Cl ₂	463	>523	—
5% Pd/δ-Al ₂ O ₃	Pd(NO ₃) ₂	473	500	15-20
5% Pd/δ-Al ₂ O ₃	Pd(NH ₃) ₄ (NO ₃) ₂	490	>493	—
10% Pd/SiO ₂	Pd(NH ₃) ₄ Cl ₂	353-358	363-368	40
10% Pd/SiO ₂	Pd(NO ₃) ₂	363-368	373-378	30-40

whatever the nature of the support (δ- or η-Al₂O₃, TiO₂), the nature of the precursor (chloride, nitrate, or tetrammine complexes), the preparation mode (impregnation or exchange), or the metal content (0.5 to 10%). This second state activity cannot be generated without contacting the catalyst with oxygen-rich reaction mixtures and the resultant activity level is equivalent to that of freshly reduced palladium-silica samples prepared by impregnation (Fig. 5); thus these Pd/SiO₂ catalysts, as such, present original features while the other samples must be transformed to produce them. A tentative explanation of this phenomenon must consider two types of assumption: the first one concerns a chemical transformation of the catalysts during the reaction at high conversion, the second has to do with the

general process of surface reconstruction.

1. *Chemical transformation.* According to Hucknall (18) and Stepanov and Margolis (19), the chemical transformations of supported silver catalysts in ethylene oxidation are especially related to the migration and elimination of surface halogens, with a subsequent rising in activity and selectivity. In a previous paper (1), we showed that a number of our catalysts contain residual chloride ions from the precursor and/or the carrier itself and XPS data indicate the presence of chlorinated surface complexes in the case of Pd/SiO₂ prepared by cation-exchange and of Pd/Al₂O₃. For Pd/Al₂O₃ the chlorine content was shown to decrease after either a pretreatment by water vapor (1) or exposure to the reaction mixture at high conversion. For Pd/SiO₂ (cation exchange), increasing the reduction temperature led to an activity enhancement (see Section I, 7) and to a significant decrease of the chlorine content (0.25 to about 0.05%). It could then be inferred that the reaction mixture is able to destroy the chlorinated complexes; this assumption is supported by the data obtained with unreduced samples prepared by impregnation from PdCl₂. Whatever the nature of the carrier (alumina, titania, silica) and the palladium content, these samples are not active below 473°K in the standard conditions (oxygen/ethylene = 5/1), in agreement with the previous

TABLE 9
XPS Data for Various PdCl₂/SiO₂
Catalysts (Impregnated)^a

Treatment	Binding energy of Pd 3d ₁ (eV)
None	338.2
Reaction mixture at the minimum detection temperature	336.2
Flowing H ₂ at 573°K for 6 hr	335.5

^a Palladium loading, 10%.

results of Kunugi and Fujimoto (20), and a second state of activity is attained as in the case of prerduced samples. In addition, XPS experiments show that a $\text{PdCl}_2/\text{SiO}_2$ sample prepared by impregnation is reduced by the reaction mixture at the minimum CO_2 detection temperature (Table 9). On the other hand, the most active catalysts in the first state are unsupported palladium (7) and freshly reduced Pd/SiO_2 (prepared by impregnation) where, according to XPS data (1), the palladium atoms have the same binding energy as in pure palladium. Thus, it is tempting to identify the activation phenomenon with a reduction of surface complexes to palladium metal. However, a second activity state was also obtained with $\text{Pd}/\eta\text{-Al}_2\text{O}_3$ catalysts which do not contain detectable amounts of residual ions (Cl^- or NO_3^-) (Section I, 6) and, on these samples too, the binding energy of palladium is very close to that of the metal (1). Thus, the reduction to metallic Pd appears to be a necessary step in the activating effect of the reaction mixture but the examination of all kinetic data suggests that another process takes place.

2. *Induced surface reconstruction.* Reconstruction phenomena have recently been invoked to account for the catalytic behavior of supported transition metals in various reactions. Taylor and co-workers (21) have shown the activities of alumina-supported Pd, Ru, or Pt in $\text{CO-H}_2\text{O}$ conversion, NH_3 synthesis, or NO reduction to be dependent on the nature of the pretreatment; a precalcination of samples led to a so-called "oxidized form" whose activity is high, whereas a prerduction induced a decrease in activity. These authors concluded that this *dual state activity* is related to a surface reconstruction during the oxygen pretreatment and/or a metal-support interaction. Working on supported Pd and Pt, Wentreck *et al.* (22) observed a continuous increase of the metal area during repeated oxygen adsorption-

CO titration cycles. They invoked a surface reconstruction induced by CO chemisorption to justify the increase of the number of sites. This phenomenon was already mentioned in other adsorption studies, especially in the presence of Pt or Ni (23). In the case of ammonia synthesis, new sites are created by stoichiometric $\text{N}_2\text{-H}_2$ mixtures (24) and the specified role of nitrogen was recognized (25). Concerning oxidation reactions, it has been known for many years that ammonia oxidation catalysts (Pt-Rh gauzes) are strongly modified upon working. A noticeable induction period occurs when all gauzes are new but this period disappears if some previously used gauzes are included in the catalytic system (26); moreover, platinum excrescences and surface enrichment in rhodium were observed at 1 atm pressure while Rh_2O_3 blankets were detected at higher pressures (27). Recent findings concerning the hydrogen-oxygen reaction over supported Pt offer striking analogies with our results; Hanson and Boudart (28) showed that, when hydrogen is in excess, the reaction is structure sensitive whereas with oxygen-rich mixtures the same reaction is structure insensitive. They proposed that corrosive chemisorption (29) of oxygen on Pt particles could erase surface anisotropies, the platinum surface becoming covered with a layer of platinum oxide. Our results demonstrate that, on the catalysts which have worked at high conversion with oxygen-rich mixtures, the activity is markedly increased (Fig. 1). As the electron microscope observation of these activated catalysts showed no redispersion of palladium, but even an increase of the particle size for well dispersed samples, i.e., ion-exchanged silica or η -alumina impregnated by $\text{Pd}(\text{NO}_3)_2$, this activity rise should not be ascribed to an increase of the number of *already existing* sites but to a change in the *nature* of the sites. This nature must now be discussed. As the activation phenomenon is observed only

with oxygen-rich mixtures, the formation of surface carbon cannot be reasonably envisaged and it should not contribute to the new sites. On the other hand, oxygen *alone* cannot be considered as responsible for the activation (cf. Section II) and it is likely that the reconstruction is induced by water or water + oxygen in the overheating conditions imposed by the olefin combustion, which are certainly more drastic than pretreating with a wet inert gas (Section II). The question arising now is whether oxygen is *present* in the reconstructed surface or whether it is only an *agent* for reconstruction. Examination by XPS and uv visible spectroscopy of catalysts after working at high conversion did not result in detection of any oxygen-enriched layer or surface compound. Hence the active surface should be metallic; in that respect, it must be recalled that water vapor was shown to induce the transformation of palladium chemically modified by the carrier into true palladium metal (1). Although it is not possible to go into details about the structure of this metal surface, it must be noted that the olefin is, partly at least, reversibly adsorbed on these new sites (Section I, 3), which should allow its conversion at a lower temperature than over the initial surface. On Pd/SiO₂ samples prepared by impregnation, the standard reducing pretreatment is able to generate such sites. In the other catalysts, the concentration of active sites is very low because the chemical state of a part of the palladium atoms is modified either by the residual anions retained by the carrier (an *indirect* metal-support interaction) or through the particular electronic properties of the carrier. The latter, which should be called a *direct* carrier effect, can account for the low activity of Pd/ η -Al₂O₃ prepared from Pd nitrate; in this catalyst, indeed, no residual anions were detected and the mean particle size (3.5 nm) is small enough to allow a significant metal-carrier inter-

action. Thus working in overheating conditions may break up the palladium-carrier interactions and induce the reconstruction of the surface, i.e., the rearrangement of the surface metal atoms.

CONCLUSION

The present study of the oxidation of ethylene over palladium catalysts first confirms that, at low conversion, significant selectivities to acetic acid may be obtained. Moreover, clear evidence is presented for the dual state behavior of these catalysts. The second state activity, obtained after working at high conversion with oxygen-rich mixtures, does not depend on the nature of the carrier and the precursor, the palladium loading, the preparation mode, or the type of pretreatment. This activation by the reaction mixture seems to arise from the destruction of the metal-carrier interactions and from a reconstruction of the palladium surface. Further information concerning the support effect are expected from an infrared study, now in course, involving the adsorption of molecular probes over palladium catalysts.

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REFERENCES

1. Bozon-Verduraz, F., Omar, A., Escard, J., and Pontvianne, B., *J. Catal.* **53**, 126 (1978).
2. Philips, G., *J. Amer. Chem. Soc.* **16**, 164 (1894).
3. Reyerson, L. M., and Swearingen, L. E., *J. Amer. Chem. Soc.* **50**, 2872 (1928).
4. Svajgl, O., and Rubas, V., *Chem. Prum.* **22**, 493 (1966); *Sb. Pr. Vyzk. Chem. Využití Uhli, Dehtu Kopy* **12**, 61 (1972); *Chem. Abstr.* **78**, 97057 (1973).
5. Kemball, C., and Patterson, W. R., *Proc. Roy. Soc. Ser. A* **270**, 219 (1962).
6. Schiefler, J., Schwentker, M., and Wicke, E., *Chem. Ing. Tech.* **45**, 990 (1973).
7. Gerberich, H. R., Cant, N. W., and Hall,

- W. K., *J. Catal.* **16**, 204 (1970); Cant, N. W., and Hall, W. K., *J. Catal.* **16**, 220 (1970).
8. Omar, A., Djega-Mariadassou, G., Bozon-Verduraz, F., and Pannetier, G., *Bull. Soc. Chim. Fr.* 2740 (1974).
 9. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8**, 348 (1967).
 10. Schwartz, A., Holbrook, L. L., and Wise, H., *J. Catal.* **21**, 199 (1971).
 11. Castellan, A., and Tauszik, G. R., *J. Catal.* **50**, 172 (1977).
 12. Bozon-Verduraz, F., and Omar, A., to be published.
 13. Close, J., and White, J., *J. Catal.* **36**, 185 (1975).
 14. Palazov, A., Chang, C. C., and Kokes, R. J., *J. Catal.* **36**, 338 (1975).
 15. Guiot, J. M., *J. Appl. Phys.* **39**, 3509 (1968).
 16. Lam, Y. L., and Boudart, M., *J. Catal.* **47**, 393 (1977).
 17. Tardy, M., and Bozon-Verduraz, F., *C. R. Acad. Sci.* **280C**, 317 (1975).
 18. Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, New York, 1974.
 19. Stepanov, Y., and Margolis, L., *Kinet. Katal.* **2**, 684 (1961).
 20. Kunugi, T., and Fujimoto, K., Proceedings of the Fifth International Congress on Catalysis (Florida 1972), p. 445, North Holland/American Elsevier, 1973.
 21. Taylor, K. C., Sinkevitch, R., and Klimisch, R., *J. Catal.* **35**, 34 (1974); Klimisch, R., and Taylor, K. C., *Environ. Sci. Technol.* **7**, 127 (1973).
 22. Wentreck, P., and Wise, H., *J. Catal.* **36**, 247 (1975); Wentreck, P., Kimoto, K., and Wise, H., *J. Catal.* **33**, 279 (1974).
 23. Poltorak, O. M., and Boronin, W. S., *Russ. J. Phys. Chem.* **40**, 11, 1436 (1966); Poltorak, O. M., Boronin, W. S., and Miltrofanova, A. N., Proceedings of the Fourth International Congress on Catalysis (Moscow 1968), Vol. II, p. 276. Akadémiai Kiadó, Budapest, 1971.
 24. Dumesic, J. A., Topsøe, H., and Boudart, M., *J. Catal.* **37**, 513 (1975).
 25. Brill, R., Richter, F. L., and Ruch, E., *Angew. Chem. Int. Ed. Engl.* **6**, 882 (1967).
 26. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
 27. Harbord, N. H., *Platinum Metals Rev.* **18**, 97 (1974).
 28. Hanson, F. V., and Boudart, M., *J. Catal.* **53**, 56 (1978).
 29. Ertl, G., and Koch, J., in Proceedings 5th International Congress on Catalysis (Florida, 1972), p. 969. North Holland/American Elsevier, 1973.