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Sulfur Poisoning and Regeneration of Palladium-based Catalysts

Part 2.†—Influence of Adsorbed Sulfur on Deactivation of Carbonaceous Deposits

Luis Javier Hoyos, Michel Primet and Hélène Praliaud*

*Institut de Recherches sur la Catalyse, Laboratoire Propre du C.N.R.S.,
Conventionné à l'Université Claude Bernard Lyon I, 2 Avenue Albert Einstein,
69626 Villeurbanne Cedex, France*

The physicochemical and catalytic properties of palladium deposited on alumina and silica–alumina have been studied after poisoning by hydrogen sulfide as well as at various stages of regeneration under hydrogen. The amount of free palladium surface atoms was mainly deduced from infrared measurements of adsorbed carbon monoxide. The catalytic activity was measured in the cyclohexane dehydrogenation. As far as the steady-state activities are concerned, a regeneration under hydrogen between 673 and 773 K leads to samples having either the same activity (alumina support) or a higher activity (silica–alumina support) compared to that of the unpoisoned catalysts. Nevertheless, in both cases, the initial metallic surface was not recovered. Pulse experiments have been used for the determination of the initial activity. They showed that the deactivation by carbonaceous deposits is hindered when sulfur is present at the surface of palladium particles. Such deactivation is favoured when palladium is supported on an acidic carrier.

In a previous paper,¹ the dehydrogenation of cyclohexane was studied on palladium supported over alumina and silica–alumina in the presence or absence of sulfur-containing compounds, *i.e.* thiophene and hydrogen sulfide. Decontamination by the feed free from sulfur as well as regenerations under hydrogen were performed. The poisoning effect was found to be of the same order of magnitude when using thiophene or hydrogen sulfide. In the case of alumina-supported noble metals the thiotolerance as well as the decontamination were smaller for palladium than for platinum. Nevertheless, the regeneration under hydrogen was more effective for Pd than for Pt. When Pd was supported on silica–alumina instead of alumina, the thiotolerance was strongly improved. Moreover after the decontamination step or regeneration under flowing hydrogen, the activity was higher than the activity measured on the fresh catalyst.

In the present paper we examine more precisely the state of the palladium supported solids after poisoning by hydrogen sulfide and regenerations under hydrogen at various temperatures. The free metal surface was determined either by the catalytic activity towards cyclohexane dehydrogenation using a feed free from sulfur or by the absorbance of the infrared bands of carbon monoxide adsorbed onto the available palladium surface atoms. After the various treatments the sulfur coverage of the palladium phase was determined after an oxidative treatment leading to the transformation of sulfur bonded to palladium into sulfate groups linked to the alumina support. The amount of sulfate species was deduced from infrared spectroscopy measurements.

Furthermore, as carbon deposits are formed at the surface of the palladium particles in the very first moments of the reaction, pulse experiments were also performed in order to determine the initial activities of fresh and of poisoned solids especially when palladium is supported on silica–alumina.

Experimental

Catalysts

The Pd/Al₂O₃ and Pd/SiO₂–Al₂O₃ solids were prepared by wet impregnation of the carriers with a known amount of palladium acetylacetonate [Pd(C₅H₇O₂)₂] dissolved in toluene.

The solvent was removed by using a rotary evaporator under reduced pressure. The solids were then dried at 383 K and calcined under a flow of oxygen at 573 K for 15 h (heating rate 2 K min⁻¹). The palladium content was thus 2.18 and 2.09 wt.% for Pd/Al₂O₃ and Pd/SiO₂–Al₂O₃ respectively. The alumina carrier was an aluminium Oxid-C from Degussa having a specific area of 100 m² g⁻¹. This alumina contains less than 20 ppm of sulfur and *ca.* 0.5 wt.% of chlorine. The silica–alumina carrier was a commercially available Ketjen LA-LPV (13% Al₂O₃, SiO₂) exhibiting a high content of sulfate impurities (0.2 wt.% of S). Its BET area was 410 m² g⁻¹.

The calcined solids were reduced overnight under a flow of hydrogen (3.6 dm³ h⁻¹) by linearly raising the temperature from 298 to 543, 673 or 773 K with a heating rate of 2 K min⁻¹.

Chemisorption Measurements and Electron Microscopy

For chemisorption measurements, the solids were outgassed at 543 or 623 K for 2 h after the reduction step and then cooled to room temperature or 348 K. Adsorption measurements were performed in a conventional volumetric apparatus. The irreversible chemisorption uptakes of hydrogen were measured at 298 K (Benson's method, dual isotherm method)² and/or at 348 K (Aben's method)³ in order to take into account the amount of hydrogen responsible for the formation of palladium hydrides. Both methods gave the same results. An adsorption stoichiometry H_{ads}/Pd_s = 1 was assumed, Pd_s being a surface palladium atom. For both catalysts, the dispersion values were also deduced from H₂–O₂ or O₂–H₂ titrations.

The reduced solids, subsequently air-contacted, were also examined by electron microscopy using a JEOL 100 CX instrument having a resolution of 0.3 nm in transmission mode.

Catalytic Activity Measurements

The procedure used for the dehydrogenation of cyclohexane (52.4 Torr† of cyclohexane in hydrogen, sample weight ranging between 5 and 15 mg, total flow rate 7.2 dm³ h⁻¹)

† Part 1: ref. 1.

† 1 Torr = (101 325/760) Pa.

into benzene, at 543 K, has been described in Part 1 of the present study.¹ Catalytic experiments were carried out in a flow system at atmospheric pressure. Reactants and products were analysed on-line by gas chromatography. In this paper, the activities are expressed per mole of cyclohexane converted into benzene per hour and per gram of palladium. For the Pd/Al₂O₃ solid the turnover number (TON) calculated taking into account the metallic area of the freshly reduced solids is also calculated.

Poisoning and Regenerations

The experiments were conducted according to the following sequence: (i) reduction in flowing hydrogen as described above, at 543, 673 or 773 K in a quartz reactor for catalytic measurements (5 to 15 mg) or in the infrared cell itself (IR pellet); (ii) cooling down to room temperature under hydrogen, evacuation 30 min at room temperature and 30 min at 373 K; (iii) introduction of hydrogen sulfide, in static conditions, at 373 K for 1 h. The quantity of H₂S was in large excess compared to the amount required for the complete sulfuration of surface palladium atoms (H₂S/Pd_s = ca. 5); (iv) evacuation of the poisoned sample, at room temperature, during 30 min; (v) regeneration overnight under a flow of hydrogen (3.6 dm³ h⁻¹) (heating rate 2 K min⁻¹) at temperatures between 543 and 773 K; (vi) cooling under flowing hydrogen to 543 K and determination of the catalytic activity towards cyclohexane dehydrogenation (reactants mixture C₆H₁₂-H₂) at the same temperature in order to measure the free palladium surface. The activities were compared with the values obtained after 1 min on stream (activity A₀) and at the steady-state (activity A_s) in the case of the freshly reduced solids. The reaction was continued for several hours.

For *in situ* IR experiments, the samples were evacuated at 543 or 623 K after the poisoning and regeneration processes described above. After recording the background spectrum, carbon monoxide was introduced at 298 K onto the evacuated samples under an equilibrium pressure close to 15 Torr. The gaseous phase was evacuated at the same temperature and a second spectrum was recorded. IR spectra were also registered after evacuation of adsorbed carbon monoxide at increasing temperature.

Determination of the Extent of Deactivation during the First Reaction Periods: Pulse Experiments

The solids (weight 10 mg) were contacted with successive cyclohexane pulses in order to determine the deactivation of the catalyst during the first stages of the reaction with the sulfur-free mixture. After reduction at the chosen temperature the solids were cooled to 543 K under H₂ and then contacted with nitrogen at the same temperature at a flow rate of 1.2 dm³ h⁻¹. Hydrogen, saturated with cyclohexane, was passed through a 0.5 cm³ pulsing loop. The partial pressure of cyclohexane (50 Torr) was controlled by adjusting the temperature of the saturator (288 K). The content of the loop was periodically introduced into the nitrogen flow passing over the catalyst maintained at 543 K. After the first introduction which corresponds to a molar ratio C₆H₁₂:Pd_s close to 3, the cyclohexane conversion was measured by gas chromatography (GC) analysis. Then a series of ten pulses was applied to the catalyst, the conversion was determined between two series of ten pulses. Between each individual pulse the sample was continuously flushed by nitrogen at 543 K. The pulse experiments were performed under computer control. By comparison with flow measurements, the amount of cyclohexane contacted with the solid after 240 pulses corresponds

to 1 min of reaction on stream. Pulse experiments have been performed on Pd/SiO₂-Al₂O₃ samples on both fresh and sulfur-contaminated solids without air contacting.

IR Spectroscopy

The samples were pressed in order to obtain thin discs of known weight. The discs were placed in a sample holder made of quartz and introduced into a cell that allowed *in situ* treatments. IR spectra were recorded at room temperature on a Fourier-transform spectrometer (I.F.S. 110 from Bruker) with a resolution of 4 cm⁻¹. Every spectrum was the sum of 100 scans. The plot function was set to absorbance.

Two kinds of spectra were obtained: (i) the IR spectra of CO adsorbed at 298 K on the freshly reduced solids and (ii) the IR spectra of CO adsorbed on the solids poisoned by H₂S at 373 K and regenerated by H₂ at various temperatures. In the absorbance spectrum, the overall integrated absorbance and the integrated absorbance for each individual band of adsorbed CO are related to the area under both bands and to the area under each band.⁴ They are obtained by graphical integration and are normalized taking into account the weight of the pellet and the palladium content. From the variations of the total integrated normalized adsorbance in the presence of sulfur it is possible to determine the fraction of free palladium.

IR spectroscopy also allows the coverage of the palladium particle by sulfur to be monitored. For this purpose, the solids, previously poisoned by H₂S, regenerated by H₂ and evacuated, were treated with oxygen in a static condition (100 Torr) at 573 K for several hours and finally evacuated at the same temperature for 1 h. The procedure allows the transformation of sulfur atoms bonded to the palladium surface atoms into sulfate species linked to the alumina support.^{5,6,7} After evacuation, the absorbance of the band at 1375 cm⁻¹, due to sulfate groups bonded to alumina, allows the determination of the coverage of palladium by sulfur.

Results

Pd/Al₂O₃

After hydrogen reduction at 673 K, the dispersion of the metallic phase is equal to 38% and corresponds to a mean particle diameter close to 3.0 nm. The dispersion values determined by H₂ chemisorption or by H₂-O₂ titrations agree well with the dispersion deduced from electron microscopy measurements. The reduction at 773 K leads to a dispersion of 35% (mean particle diameter of 3.2 nm). From chemical analysis, the sulfur content of the solid is smaller than 19 ppm (wt.) whereas the chlorine content reaches 0.3 wt.%. The carbon content does not exceed 0.1 wt.%.

IR Spectra of CO adsorbed on the Freshly Reduced Pd/Al₂O₃

Fig. 1 shows the IR spectra of CO irreversibly adsorbed between 298 and 523 K on the alumina-supported palladium solid reduced at 673 K. Palladium is completely reduced since no IR bands attributed to CO adsorbed on ionic palladium were evidenced. The well known spectrum of CO adsorbed on metallic palladium is observed,⁸⁻¹¹ i.e. a high-frequency band (HF) at 2065 cm⁻¹ and low-frequency bands (LF) at 1980 cm⁻¹ and 1930 cm⁻¹ (shoulder). The HF band is associated with linearly bonded CO (L) whereas multiple coordinated CO (B) gives rise to bands in the LF region. The LF bands at 1980 and 1930 cm⁻¹ are sometimes more precisely attributed to bridged CO species adsorbed on the (100) and (111) faces of palladium crystallites, respectively.^{9,12} The positions of the bands are not strongly affected by the reduction temperature (673 or 773 K).

Fig. 1 IR spectra of carbon monoxide chemisorbed on Pd/Al₂O₃ reduced at 673 K and evacuated at 623 K (or 673 K): (a) CO irreversibly adsorbed at 298 K; (b) after evacuation at 423 K; (c) after evacuation at 523 K

The percentage of linear species is given by the ratio $\mathcal{A}_L/(\mathcal{A}_L + \mathcal{A}_B)$, $\mathcal{A}_L$ being the absorbance of the HF band (linearly bonded carbon monoxide) and $\mathcal{A}_B$ the absorbance of the LF bands (multibonded carbon monoxide). It is equal to 13% after reduction at 673 K and to 9% after reduction at 773 K (Table 1). Among the B bands associated to multi-coordinated CO, the 1980 cm⁻¹ band is clearly predominant (62% of the absorbance of the LF bands). The overall integrated corrected absorbance which is normalized taking into account the weight of palladium is close to 0.82 (arbitrary units) after reduction at 673 K and 0.83 after reduction at 773 K (Table 1). No variation in the absorbance of the $\nu(\text{CO})$ bands is observed for the two reduction temperatures since both the dispersion and the $\mathcal{A}_L/(\mathcal{A}_L + \mathcal{A}_B)$ ratio are not strongly affected by the reduction temperature.

As the evacuation temperature of the CO covered Pd/Al₂O₃ sample increases, the linear species disappear between 373 and 423 K whereas the multibonded species disappear at higher temperature (573 K). The position of the LF bands is coverage dependent with a downwards frequency shift, the carbon monoxide coverage decreasing because of the increase in the evacuation temperature. After a vacuum treatment at 523 K, the bands initially present at 1980 and

1930 cm⁻¹ are situated at 1895 and 1805 cm⁻¹, respectively (Fig. 1). The shift in the position of the bands due to multi-bonded CO could be caused either by the decrease of the vibrational coupling of carbon monoxide adjacent dipoles^{13,14} or by changes in the coordination state of adsorbed CO because of the presence of various crystal planes.^{9,12}

IR Spectra of CO adsorbed on Sulfur-poisoned Pd/Al₂O₃ Samples

The treatment by H₂S at 373 K followed by a regeneration under hydrogen at various temperatures produces changes in the spectrum of adsorbed CO (Fig. 2).

The band corresponding to CO linearly bonded to palladium is shifted towards higher wavenumbers. For instance, after a generation at 573 K, the $\nu(\text{CO})$ band is located at 2080 cm⁻¹. After a regeneration at 673 K, two bands at 2080 and 2060 cm⁻¹ are observed. The strength of the C—O bond is increased, so the Pd—CO bond is weakened. Such behaviour cannot be explained by a decrease in the CO coverage which would lead to a small downwards frequency shift. It is generally explained by a decrease in the back donation of the

Fig. 2 IR spectra of carbon monoxide irreversibly adsorbed at 298 K on the Pd/Al₂O₃ sample reduced at 673 K and evacuated at 623 K: (a) After treatment by H₂S at 373 K and regeneration under flowing hydrogen at 573 K; (b) after treatment by H₂S at 373 K and regeneration under flowing hydrogen at 673 K

Table 1 IR data concerning CO adsorbed on freshly reduced and sulfur-poisoned samples

sample	reduction temperature /K	regeneration temperature /K	A	$100 \cdot \mathcal{A}_L/(\mathcal{A}_L + \mathcal{A}_B)$ (%)	accessible Pd _s (%)
Pd/Al ₂ O ₃	673	no H ₂ S	0.82	13	100
	773	no H ₂ S	0.83	9	100
	673	573	0.21	22	26
	673	673	0.39	16	48
	773	773	0.55	13	73
Pd/SiO ₂ -Al ₂ O ₃	543	no H ₂ S	0.93	11	100
	673	no H ₂ S	0.65	24	100
	543	543	0.20	33	21
	673	673	0.58	26	89

Accessible Pd_s: Fraction of palladium surface atoms accessible to CO determined by IR spectroscopy as the ratio of the A values for sulfur-poisoned and clean solids.

metal electrons to the $2\pi^*$ antibonding CO orbitals. An electron transfer from Pd to S (electron acceptor) is probably occurring and the corresponding $\nu(\text{CO})$ frequency increases. It has already been reported that the M—S bond is partially ionic leading to an electron transfer from Pd atoms to S adatoms.¹⁵

The position of the LF bands is strongly modified (Fig. 2) with a downwards frequency shift, from 1980 to 1925 cm^{-1} and from 1930 to 1855 cm^{-1} when going from the fresh solid (Fig. 1) to the solid poisoned by H_2S and regenerated at 573 K (Fig. 2). This phenomenon might be explained by a decrease in the CO coverage.^{13,14}

According to the upward shift of the HF band, sulfur poisoning would lead to a decrease in the electron density of the Pd surface atoms. The multi-bonded CO species (LF bands) are more sensitive to the coverage effects, which leads to a downwards frequency shift, than the linearly bonded ones (HF band). Thus an electronic effect due to the presence of adsorbed sulfur adatoms cannot be evidenced for the LF bands.

Upon evacuation at increasing temperatures the HF band disappears at around 373 K and the LF bands disappear at 473 K, i.e. at lower temperatures than the corresponding bands observed on the fresh solid. On the poisoned solid the chemisorbed CO species are less stable than on the initial solid, the strength of the Pd—CO bond has been weakened. The change in the thermal stability of adsorbed CO is in good agreement with HF shift of the band corresponding to linear CO.

The fraction of CO linearly bonded to Pd^0 increases in the presence of adsorbed sulfur (Table 1). This increase is stronger for low regeneration temperatures. Such behaviour is not related to an increase in the metal dispersion since no change in the palladium particle size was evidenced by TEM after hydrogen sulfide adsorption. This result suggests that surface palladium atoms become isolated one from another (dilution effect) by the presence of sulfur, as it has been already reported in the literature.^{6,7,16} Pre-adsorbed sulfur does not form islands or patches but seems to be homogeneously distributed over the surface of the palladium particles.

The overall integrated normalized absorbance, $\mathcal{A}$, clearly decreases in the presence of sulfur. The decrease is more pronounced for low regeneration temperatures than for high ones. The percentage of free palladium accessible to CO is determined by the ratio of the $\mathcal{A}$ values for sulfur contaminated solids to those measured for fresh solids (Table 1). The determination of the percentage of free palladium surface from the overall integrated absorbance has been performed with the assumption that intensity changes in the $\nu(\text{CO})$ IR bands are directly related to concentration changes.

Even after a regeneration under hydrogen at 773 K the initial metallic surface accessible to CO is not completely restored in spite of recovering a percentage of the linear form. Such a behaviour could suggest the formation of sulfur islands during the regeneration process under hydrogen.

Treatments under Oxygen

After poisoning by H_2S and regeneration by H_2 of the $\text{Pd}/\text{Al}_2\text{O}_3$ solid, oxygen treatments at 573 K lead to the transformation of sulfur bonded to Pd^0 into sulfate groups linked to the alumina support. These species are characterized by a band at 1375 cm^{-1} . Evacuation at 573 K does not modify the intensity of the 1375 cm^{-1} band whereas the sulfate species are partially reduced by treatment under hydrogen at the same temperature. However even after a treatment by H_2 at 773 K, the band due to sulfate groups bonded to alumina does not totally disappear from the IR

spectrum (the absorbance decrease reaches only 60%) in contrast to previous studies on $\text{Pt}/\text{Al}_2\text{O}_3$ samples.^{6,7}

A calibration has been performed previously in order to correlate the absorbance of the 1375 cm^{-1} band (normalized surface area under the band) with the amount of sulfate present in the sample.⁷ According to the calibration curve,⁷ the amount of sulfur contained in each poisoned sample has been determined. The results are given in Table 2. It is possible to calculate the S : Pd_s ratio, taking into account the dispersion determined by H_2 chemisorption on the unpoisoned sample. Such a calculation requires that the sulfur atoms adsorbed on palladium particles are completely oxidized into sulfate groups bonded to the support by the treatment under oxygen at 573 K. The evolution of the S/ Pd_s ratios is similar to that of the integrated normalized absorbances $\mathcal{A}$, i.e. the number of Pd_s accessible to CO increases when the sulfur content decreases. The ratio of the poisoned palladium surface fraction inaccessible to CO (Table 1) to S/ Pd_s (Table 2) is designated $\Delta\text{CO}/\Delta\text{S}$ and is given in Table 2. This ratio is larger than unity. As a consequence, CO chemisorption would require larger ensembles than sulfur chemisorption. Note, however, that the quantitative comparisons here performed imply that the IR spectra of adsorbed CO are not qualitatively changed or that the molar absorption coefficients of the bands corresponding to the various species are the same in the presence and in the absence of adsorbed sulfur.

Catalytic Activities of Fresh and Poisoned $\text{Pd}/\text{Al}_2\text{O}_3$

The catalytic activities of the samples poisoned by H_2S and regenerated by hydrogen treatments at increasing temperatures were measured in the cyclohexane dehydrogenation (sulfur free mixture $\text{C}_6\text{H}_{12}-\text{H}_2$) at 543 K and compared to the activities of the fresh catalysts.

The activities were measured after 1 min on stream and the reaction continued for several hours. The activities are compared to the initial activity A_0 [3.85 mol $\text{g}(\text{Pd})^{-1} \text{h}$] (turnover number $N_0 = 1078 \text{ h}^{-1}$) measured after 1 min and to the steady-state activity A_{st} [3.7 mol $\text{g}(\text{Pd})^{-1} \text{h}^{-1}$] obtained in the same conditions on the clean solid.¹ Note that these values are known with an accuracy of 5% (Table 3). For the freshly reduced solid the decrease in activity observed between 1 min on stream and the steady state is equal to ca. 4–5%. It is attributed to carbon deposition.

Fig. 3 gives the percentage of regeneration as a function of the temperature of hydrogen treatment. This percentage is expressed by the ratio of the steady-state activity of the regenerated solid to that of the freshly reduced one. After poisoning by H_2S and treatment with H_2 at 543 K, the regeneration increases from 12 to 25% between 1 and 180 min on stream. For the regenerations at higher temperatures the activity is stable after 1 min.

After treatment with H_2 at ca. 650 K the catalyst recovers its activity A_{st} in spite of the presence of remaining adsorbed sulfur and the fact that the initial metallic surface accessible to CO is not fully restored. The initial activity A_0 is not restored. The regenerations under flowing hydrogen after the

Table 2 Amount of sulfur contained in poisoned $\text{Pd}/\text{Al}_2\text{O}_3$ samples; comparison with the Pd surface accessible to CO

reduction temperature /K	regeneration temperature /K	amount of S /ppm $\text{g}(\text{solid})^{-1}$	S : Pd_s	$\Delta\text{CO}/\Delta\text{S}$
673	573	1240	0.5	1.5
673	673	560	0.22	2.4
773	773	370	0.16	2.1

Table 3 Catalytic activities expressed in $\text{mol g(Pd)}^{-1} \text{ h}^{-1}$ of cyclohexane converted into benzene for fresh samples and for H_2S poisoned samples regenerated under hydrogen. A_0 , A_{180} and A_{400} being the activities measured for 1, 180 and 400 min on stream respectively

catalyst	A_0	A_{180}	A_{400}
$\text{Pd/Al}_2\text{O}_3$			
fresh	3.85 ± 0.2	3.70 ± 0.2	3.70 ± 0.2
$\text{H}_2\text{S-H}_2$ 543 K	0.45	0.9	
$\text{H}_2\text{S-H}_2$ 573 K	1.3	1.3	
$\text{H}_2\text{S-H}_2$ 673 K	3.7	3.7	
$\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$			
reduced 673 K			
fresh	6.5 ± 0.6	5.4 ± 0.5	5.4 ± 0.5
$\text{H}_2\text{S-H}_2$ 543 K	4.4 ± 0.3	5.7 ± 0.6	6.7 ± 0.5
$\text{H}_2\text{S-H}_2$ 573 K	6.9 ± 0.6	5.6 ± 0.6	6.6 ± 0.5
$\text{H}_2\text{S-H}_2$ 673 K	7.0 ± 0.7	6.3 ± 0.6	—
reduced 543 K			
fresh	6.5 ± 1	6 ± 1	6 ± 1
$\text{H}_2\text{S-H}_2$ 543 K	4.7 ± 1	6 ± 0.2	7.4 ± 0.03

For the freshly reduced solids the activity A_{180} is equal to the steady-state activity A_{st} .

treatment by H_2S are similar to those observed after poisoning by H_2S or thiophene during the catalytic reaction in the presence of a sulfur contaminated mixture ($\text{C}_6\text{H}_{12}\text{-H}_2\text{-H}_2\text{S}$ or $\text{C}_6\text{H}_{12}\text{-H}_2\text{-C}_4\text{H}_4\text{S}$).¹

$\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$

The palladium dispersion values determined by hydrogen chemisorption (Benson or Aben's methods) are *ca.* 13 and 6% after reduction at 543 and 673 K respectively. The corresponding mean particle diameters (8.5 and 18.5 nm) are larger than the diameters deduced from electron microscopy measurements (4.7 and 5.4 nm). The sulfate groups initially present on the silica-alumina support have been reduced to hydrogen sulfide which poisons the palladium surface atoms. The number of sulfate groups reduced to sulfide groups, *i.e.* the extent of the poisoning, increases with the reduction temperature. The palladium dispersion values deduced from H_2 titration of adsorbed O_2 are higher than the values obtained by H_2 chemisorption; they reach 27 and 20% after reduction at 543 and 673 K respectively.¹ It is likely that a part of the sulfur located on the palladium surface atoms after the H_2 reduction has been oxidized by O_2 at room temperature into SO_x species bonded to the metal particles. Such species

Fig. 3 Percentage regeneration of the catalytic activity after treatment by H_2S and regenerations under flowing hydrogen at various temperatures for the $\text{Pd/Al}_2\text{O}_3$ previously reduced at 673 K. The activities here reported are measured at the steady states

would be responsible for the increase of H_2 consumption during the titration of adsorbed O_2 . Since the dispersion of the $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$ solid remains ambiguous the catalytic activities reported here will be expressed per g of palladium.

After reduction at 673 K the sulfur, chlorine and carbon contents are 0.12, 0.21 and 0.16 wt.%, respectively.

IR Spectra of CO Adsorbed on the Freshly Reduced $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$

The IR spectrum of CO irreversibly adsorbed at 298 K on $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$ reduced at 543 K [Fig. 4(a)] is slightly different from that observed for the alumina-supported palladium solid reduced at 673 or 773 K (Fig. 1). For instance, the HF band corresponding to linear adsorbed CO is broad, between 2090 and 2070 cm^{-1} . The LF band observed at 1980 cm^{-1} in the case of the alumina support is now located at 1960 cm^{-1} . It is possible to consider that some poisoned Pd atoms (band at 2090 cm^{-1}) coexist with the free Pd atoms (band at 2070 cm^{-1}) but the fraction of poisoned Pd_s remains weak owing to the presence of the 1960 cm^{-1} band. The reduction of the sulfate impurities of the support remains moderate at 543 K.

As the reduction temperature increases from 543 to 673 K the spectrum is strongly modified, the HF and the LF bands are now located at 2090 and 1935 cm^{-1} respectively [Fig. 4(b)]. The spectrum is similar to the spectrum observed after treatment by H_2S and regeneration by H_2 at 673 K for the $\text{Pd/Al}_2\text{O}_3$ sample (Fig. 2). Such changes in the IR spectra are due to the reduction, at 673 K, of the sulfate impurities initially present on the silica-alumina support. This reduction leads to the formation of hydrogen sulfide which poisons the metal particles. The position of the HF band at 2090 cm^{-1} may be related to an electron-deficient character of the palladium due either to the acidic support itself or to the presence of sulfur atoms bonded to the surface metal atoms. At the same time, the percentage of linearly bonded CO increases whereas the overall integrated absorbance decreases (Table 1).

Upon evacuation at increasing temperatures, when the $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$ solid is reduced at 673 K, the multibonded CO species disappear at 473 K, *i.e.* at lower temperatures than for the $\text{Pd/Al}_2\text{O}_3$ solid. The Pd-CO bond strength would be weaker as suggested by the electron-deficient character of surface palladium atoms.

IR Spectra of CO adsorbed on the Sulfur-poisoned $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$

The effect of H_2S poisoning depends on the reduction temperature. For the $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$ sample reduced at 543 K,

Fig. 4 IR spectra of CO irreversibly adsorbed at 298 K on the $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3$ sample: (a) reduction at 543 K and evacuation at 543 K; (b) reduction at 673 K and evacuation at 623 K

Fig. 5 IR spectra of CO irreversibly adsorbed at 298 K on a Pd/SiO₂-Al₂O₃ sample after treatment by H₂S at 373 K and regeneration under flowing hydrogen: (a) reduction and regeneration at 543 K; (b) reduction and regeneration at 673 K

sulfur poisoning by H₂S produces changes similar to those obtained for Pd/Al₂O₃ (Fig. 2 and 5). The band corresponding to the CO linear species is observed at high frequency and the bands corresponding to multi-bonded CO species at low frequencies. The percentage of linearly bonded CO increases when the fraction of Pd⁰ accessible to CO decreases (Table 1). As for the alumina support, in the presence of pre-adsorbed sulfur, an electron-deficient character of the Pd atoms and a dilution by the sulfur atoms occur.

For the Pd/SiO₂-Al₂O₃ sample reduced at 673 K in which the metallic phase is already completely poisoned the introduction of H₂S does not modify the IR spectrum. The positions of the bands are unaffected, the $\mathcal{A}$ value and the percentage of linear species are only slightly modified.

Oxygen treatments at 573 K do not lead to the formation of sulfate groups bonded to the support. It is suggested, in opposition with the alumina support, that SO₂ or SO₃ formed by oxidation of sulfur atoms bonded to palladium do not interact with an acidic support such as silica-alumina.

Catalytic Activities of Fresh and Poisoned Pd/SiO₂-Al₂O₃

After poisoning by H₂S and treatment under flowing hydrogen the activities are measured in the presence of a sulfur-free (C₆H₁₂-H₂) mixture. For a freshly reduced solid at 543 K the initial activity A_0 measured after 1 min on stream is equal to

Fig. 6 Pulse experiments: determination of the initial activities of the Pd/SiO₂-Al₂O₃ solid. C_i is the cyclohexane conversion for the i th pulse: (a) solid freshly reduced at 543 K; (b) solid freshly reduced at 673 K; (c) solid reduced at 673 K, treated with H₂S at 373 K and regenerated under hydrogen at 573 K

6.5 mol g(Pd)⁻¹ h⁻¹ and decreases to a steady-state level $A_{st} = 6.0$ mol g(Pd)⁻¹ h⁻¹ after 3 h on stream. The deactivation reaches 9%. For the sample reduced at 673 K these values are 6.5 and 5.4 mol g(Pd)⁻¹ h⁻¹ respectively and the deactivation is equal to 16%.¹ The presence of an acidic support favours the deactivation by coking.¹⁷ Owing to the low weight of Pd/SiO₂-Al₂O₃ solid, between 5 and 8 mg, used to achieve a low conversion at 543 K and to avoid diffusion, the accuracy of the measurements is lower than in the case of the Pd/Al₂O₃ solid. The activity measured at 1 min on stream is especially inaccurate; it is known to within 10% (reduction at 673 K) and 16% (reduction at 543 K) (Table 3).

For the solids treated by H₂S and regenerated under hydrogen the activities obtained after 1 min (A_0), 180 and 400 min (A_{180} and A_{400}) are reported on Table 3. The activities A_0 are known to within 10–20%. By comparison with the clean solids an overactivity is observed. The ratios of the activities measured after 400 min on stream for sulfur-contaminated and fresh samples reach around 1.2 for all the Pd/SiO₂-Al₂O₃ solids here studied. This overactivity is similar to that observed after poisoning by a sulfur contaminated mixture (C₆H₁₂-H₂-H₂S or C₆H₁₂-H₂-C₄H₄S) at 543 K. In this latter case the removal of the sulfur contaminant from the feed or a treatment under flowing hydrogen at 543 K leads to an overactivity (factor 1.4) by comparison with the steady-state activity of the fresh solid reduced at 673 K.¹

When the regenerations under H₂ are performed at 543 K the activities in the presence of the sulfur-free mixture increase with time, as noticed for the Pd/Al₂O₃ solid. When the regenerations are performed at 573 and 673 K the activities decrease with time but the deactivation is smaller for the poisoned solids than for the fresh ones. It is difficult to consider that the treatment at 543 K by the mixture C₆H₁₂-H₂ is more efficient than the treatment by H₂ alone. It is likely that the regeneration at 543 K would be very slow and consequently not achieved after one night of hydrogen treatment.

Deactivation during the First Periods of Reaction with Sulfur-free Mixtures

The pulse experiments allow one to determine the extent of deactivation which is occurring during the first moments on stream with the sulfur-free mixtures. Carbon deposits are formed as soon as the solids are contacted with the cyclohexane-hydrogen mixture since the amount of benzene formed decreases strongly between the first pulse and the 240th pulse. This latter corresponds to the amount of cyclohexane fed to the catalyst after 1 min on stream. For the following pulses, the activity decrease is less pronounced (Fig. 6).

The activities A_0 determined after 1 min on stream differ strongly from the initial activities, especially for the fresh solids not contacted with H₂S. For the fresh solid reduced at 543 K the ratio R of the activities measured at the 240th pulse and at the first pulse reaches 0.55. This ratio R becomes equal to 0.71 when the fresh solid is reduced at 673 K, i.e. when the poisoning of the metal particles by the hydrogen sulfide arising from the reduction of the sulfate impurities of the support increases. The deactivation is still less pronounced after treatment by H₂S. The ratio R becomes equal to 0.91 for the solid reduced at 543 K, treated by H₂S at 373 K and regenerated under hydrogen at 543 K. It is equal to 0.83 for the solid reduced at 673 K, poisoned and regenerated under hydrogen at 573 K.

The deactivation by carbon residues is less pronounced in the presence rather than the absence of preadsorbed sulfur. Sulfur atoms remaining adsorbed on the metal particles inhibit the formation of carbonaceous residues since their formation requires an ensemble of several surface atoms.^{18–21}

Discussion and Conclusion

In this work concerning alumina- and silica-alumina-supported Pd solids, the infrared spectroscopy of adsorbed CO has allowed us to determine the free Pd surface accessible to CO after poisoning by hydrogen sulfide and after regeneration under flowing H_2 at various temperatures. The CO probe molecule also allows the detection of possible variations in the electronic properties of the metal after poisoning. After oxidation at 573 K of the sulfur atoms bonded to the Pd surface atoms, the absorbance of the IR band at 1375 cm^{-1} corresponding to the sulfate groups linked to Al_2O_3 allows us to determine the total amount of sulfur contained in each sample.

For the Pd/ Al_2O_3 solid, in the presence of sulfur, the surface accessible to CO is decreased and the properties of the metal are modified. Even after regeneration under H_2 at 773 K the initial metallic surface accessible to CO is not restored and the solid contains some sulfur atoms oxidizable into sulfate groups. After the regeneration at various temperatures the percentages of free Pd_s accessible to CO and the S: Pd_s ratio are calculated. The comparison of these two values shows that the CO chemisorption requires larger ensembles than the sulfur chemisorption.

In the presence of sulfur the band corresponding to CO linearly bonded to Pd⁰ is shifted towards higher wavenumbers and the thermal stability of the chemisorbed CO species is decreased. So the strength of the Pd—CO bond is weakened because of an electron transfer from Pd to S. Furthermore the sulfur is homogeneously distributed among the surface of the particles, leading to a dilution effect increasing the fraction of CO linearly bonded to Pd⁰.

With the silica-alumina support the presence of sulfur bonded to Pd⁰ induces similar effects than with alumina, i.e. electron-deficient character of the Pd surface atoms with a weakening of the Pd⁰—CO bond and dilution by the sulfur atoms. Such an effect can be induced by reduction at 673 K of the sulfate impurities initially present on the silica-alumina support.

In spite of the presence of sulfur atoms on the contaminated Pd/SiO₂—Al₂O₃, hydrogen treatments lead to overactivities by comparison with the steady-state activity and with the activity measured after 1 min on stream. Pulse experiments have allowed the determination of the deactivation extent in the presence of C₆H₁₂—H₂ mixtures free of sulfur. They evidence an important coverage of the metallic surface by carbonaceous residues during the first moments of the reaction. For instance, for the fresh Pd/SiO₂—Al₂O₃ solid reduced at 543 K, the activity measured after 1 min on stream differs by 45% (ratio 0.55) from the initial activity. For the sample poisoned by hydrogen sulfide and partially regenerated by hydrogen treatment at 543 K the amount of carbonaceous deposits formed during the first minutes of reaction is strongly decreased, the activity measured after one minute on stream differs only by 10% from the initial activity. In the case of the fresh Pd/SiO₂—Al₂O₃ sample reduced at 673 K, the partial reduction of the sulfate species linked to the support leads to a poisoning of the metallic phase. The deactivation by carbonaceous deposits during the first moments of reaction is inferior to the deactivation observed with the solid reduced at 543 K because of the presence of preadsorbed sulfur on the surface of palladium particles. The activity measured after 1 min on stream differs by 28% (ratio 0.72) from the initial activity. A subsequent poisoning by H₂S and a regeneration under hydrogen at 573 K still lowers the formation of carbon deposits but does not inhibit them totally. As a consequence, preadsorbed sulfur has no promoting effect on the initial activity of palladium in the reac-

tion of cyclohexane dehydrogenation. On the contrary, the catalytic activity is decreased in the presence of sulfur adatoms bonded to the metallic surface. Nevertheless, the partial coverage of palladium particles by sulfur is responsible for the reduction of carbonaceous deposits responsible for the catalyst deactivation in the course of reaction with a sulfur-free mixture.

The introduction of small amounts of sulfur is known to improve selectivity and activity because of the suppression of the high dehydrogenation activity of the metal responsible for the formation of coke precursors.^{22,23} Nevertheless, an increase in the sulfur metal particles coverage leads to sulfur poisoning.²²

In the case of Pd/ Al_2O_3 , IR experiments show that the metallic surface is still partially sulfur covered after regeneration under hydrogen at ca. 650 K although the steady-state activity is fully restored. The initial activity measured after 1 min on stream is not restored. The presence of carbonaceous deposits formed during the very first moments of the reaction is also possible, although probably to a lower extent than with a more acidic support. A similar role of preadsorbed sulfur could be expected i.e. lowering of the amount of deposited carbon during the reaction with a sulfur-free mixture.

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