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Sulfur Poisoning and Regeneration of Palladium-based Catalysts

Part 1.—Dehydrogenation of Cyclohexane on Pd/Al_2O_3 and Pd/SiO_2–Al_2O_3 Catalysts

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The catalytic activity of palladium deposited on alumina and silica–alumina for the dehydrogenation of cyclohexane was studied. The introduction of sulfur-containing compounds, thiophene or hydrogen sulfide into the feed, was investigated.

The Pd/Al_2O_3 catalyst was less active than platinum deposited on alumina for cyclohexane aromatization in the absence of any poisoning additive. In addition, the thio-tolerance is smaller for palladium than for platinum. The decontamination by the sulfur-free feed was also less efficient in the case of alumina supported palladium. However, regeneration under pure hydrogen was more effective for the Pd/Al_2O_3 sample than for the Pt/Al_2O_3 one.

When palladium was supported on silica–alumina instead of alumina, the deactivation by coking was more intense for sulfur-free reactants. Nevertheless the thio-tolerance was strongly improved in comparison with the Pd/Al_2O_3 catalyst. In contrast to iridium and platinum supported on silica–alumina, previously studied under similar conditions in the literature, the removal of thiophene or hydrogen sulfide from the feed allowed a total recovery of the catalytic activity of the Pd/SiO_2–Al_2O_3 sample. The sample regeneration was observed after treatment under flowing hydrogen. Such behaviour is discussed in terms of changes of coke precursor reactivity in the presence of adsorbed sulfur.

Sulfur is the major common element which readily forms compounds with metal catalysts and most catalytic processes must take place at extremely low levels of sulfur contamination. The poisoning by sulfur has been the subject of numerous studies, analysed in several review articles.[1–5] Most of the work deals with Ni, Pt and Ir. Catalytic control of the pollutants (hydrocarbons, carbon monoxide, nitrogen oxides) in automobile exhaust requires the use of catalysts resistant to thermal variations and to poisoning by various pollutants such as P, Pb, S, Zn *etc* Palladium is capable of simultaneously converting significant quantities of hydrocarbons, carbon monoxide and nitrogen oxides and, in an oxidizing atmosphere is more resistant to sintering than platinum.[6,7] Its resistance to poisoning, in particular by sulfur compounds, seems less extensively studied than that of platinum.

In this paper the extent of the contamination of palladium supported solids by sulfur compounds is followed with the help of a so-called structure-insensitive reaction, the dehydrogenation of cyclohexane, either pure or containing thiophene or hydrogen sulfide. The possibility of recovering the activity after poisoning by thiophene or H_2S, in the presence of the pure mixture or by contacting with H_2 is examined. A comparison with the other metals, especially Pt and Rh, commonly used in automotive catalytic convertors is made. The influences of chlorine in the support or in the precursor, of sulfur in the support, of the nature of the support (alumina or silica–alumina), and of the dispersion are examined.

Experimental

Preparation of the Solids

Two solids from a chlorine-free palladium precursor (palladium acetylacetonate) have been prepared, using alumina and silica–alumina as supports. However, for comparison others solids have also been used. The solids prepared are listed in Table 1.

A non-microporous alumina (aluminium Oxyd-C from Degussa) (B.E.T. area 100 m^2 g^{-1}) was used as the carrier. This alumina contains less than 20 ppm of sulfur but contains *ca.* 0.5 wt.% of chlorine. In order to avoid the presence of chlorine, known to be an important modifier of catalytic systems, another alumina carrier, chlorine-free, has also been studied, the alumina SCM-129, commercially available from Rhône-Poulenc. Its B.E.T. area is 107 m^2 g^{-1} and it contains sulfur (between 150 and 200 ppm of S). The commercially available silica–alumina carrier Ketjen LA-LPV (13% Al_2O_3, SiO_2) exhibits a high content of sulfate impurities (0.2 wt.% of S) liable to interfere with the metallic phase especially during the reduction process. Its B.E.T. area was 410 m^2 g^{-1}. Before contacting with the palladium salt the silica–alumina carrier was calcined under oxygen at 873 K for 24 h.

In the case of the $Pd(C_5H_7O_2)_2$ precursor, the solids were prepared by wet impregnation of the carriers with a known amount of the salt dissolved in toluene.[8] The solvent was

Table 1 Catalysts studied in the present work

catalyst	support	noble metal precursor	metal (wt.%)
Pd/Al_2O_3I	Al_2O_3 Degussa	$Pd(C_5H_7O_2)_2$	2.18
Pd/Al_2O_3II	Al_2O_3 RP SCM 129	$Pd(C_5H_7O_2)_2$	1.96
Pd/Al_2O_3 III	Al_2O_3 RP SCM 129	H_2PdCl_4	1.98
Pt/Al_2O_3	Al_2O_3 RP SCM 129	H_2PtCl_6	2.05
Rh/Al_2O_3	Al_2O_3 RP SCM 129	$RhCl_3$	1.94
Pd/SiO_2–Al_2O_3	SiO_2–Al_2O_3 Ketjen LA-LPV	$Pd(C_5H_7O_2)_2$	2.09

removed by using a rotary evaporator under reduced pressure. The sample was dried overnight at 383 K then calcined under a flow of oxygen at 573 K for 15 h with a heating rate of 2 K min^{-1}.

The palladium chloride precursor was dissolved in an excess of concentrated hydrochloric acid in order to form the H_2PdCl_4 compound. Excess HCl and water were eliminated under reduced pressure and the solid obtained dissolved in water. The Pd/Al_2O_3 solid was thus prepared by impregnation with the aqueous H_2PdCl_4 solution. After drying it was calcined under a flow of nitrogen at 773 K for 2 h.

Platinum was introduced by using an aqueous solution of H_2PtCl_6 using the classical incipient wetness impregnation procedure.[9] After drying at 283 K for 10 h, they were calcined for 1 h at 773 K under flowing nitrogen.

Rhodium was introduced by impregnation with the $RhCl_3$ salt in aqueous solution and the solid thus obtained dried and calcined under nitrogen at 773 K for 1 h.

Before reduction the Pd/Al_2O_3 I solid (alumina from Degussa and palladium acetylacetonate) was treated at high temperatures, at 1173 K, in an oxidizing atmosphere (1.5 vol.% oxygen in nitrogen) in the presence of water (10%) in the flow, leading to the obtention of the so-called Pd/Al_2O_3 I′ solid. The following conditions were used: 0.5 g solid, flow rate 20 dm^3 h^{-1}, heating rate 5 K min^{-1}, plateau 10 h. There is no loss of palladium during this process. The B.E.T. area was decreasing from 102 to 87 m^2 g^{-1}.

The calcined solids were reduced overnight in a flow of hydrogen (3.6 dm^3 h^{-1}) by linearly raising the temperature up to the required value (673 K in the case of the alumina-supported solids) at the heating rate of 2 K min^{-1}. For the $Pd/SiO_2–Al_2O_3$ solids two reduction temperatures were used, 543 and 673 K, since it is known that sulfate contamination does not generally affect the metal properties for reduction temperatures lower than 573 K. After hydrogen treatment at 673 K the sulfate groups contained in the support are reduced to hydrogen sulfide which poisons the metal.[10,11,12] Under these reduction conditions the samples were completely reduced (no IR bands of carbon monoxide adsorbed on palladium in an oxidized state).

Chemisorption Measurements and Electron Microscopy

Hydrogen chemisorption measurements were performed in a classical volumetric apparatus at room temperature on the solid outgassed at 623 K. The irreversible chemisorption uptakes of hydrogen were measured by using the dual-isotherm technique: after the determination of the first isotherm the samples were evacuated at 298 K for 20 min and a second isotherm was determined. In the case of palladium a chemisorption at 348 K was also performed in order to avoid hydride formation and to verify the volume of irreversibly adsorbed hydrogen measured at 298 K. The dispersion was calculated assuming an adsorption stoichiometry $H_{ads}/M_s = 1$ where M_s is a surface metal atom. Dispersion was also deduced from the quantity of oxygen used to titrate hydrogen irreversibly adsorbed or from the quantity of hydrogen used for the titration of adsorbed oxygen. The agreement between the values deduced from the various methods was good.

Direct observations of the samples (TEM) were made using a JEOL 100 CX microscope (resolution 0.3 nm), reduced samples being dispersed in anhydrous ethanol by ultrasound and a drop of the suspension being deposited on a carbon-coated copper grid.

Catalytic Activity Measurements

The procedure used for the dehydrogenation of either sulfur-free or sulfur contaminated (thiophene or H_2S) cyclohexane to benzene has been described previously.[13–17] After reduction the solids were cooled down to the reaction temperature (543 K). The experiment was divided into three phases. No air was admitted to the system during all the experiment. Fig. 1 shows a typical catalytic run for the Pd/Al_2O_3 I solid.

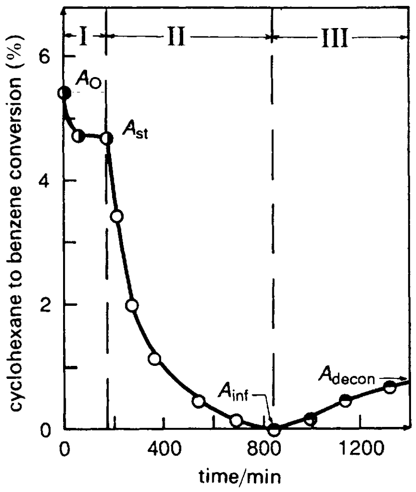

Fig. 1 Typical catalytic run for the solid Pd/Al_2O_3 I reduced at 673 K. The catalytic activity was measured at 543 K. Reactants: cyclohexane, hydrogen. Presence of thiophene in phase II. I: phase I, II: phase II, III: phase III

During phase I the catalyst was contacted with hydrogen and pure cyclohexane (52.4 Torr† of cyclohexane, thermostatted bath at 285 K). The initial activity, after 1 min of contact with the reaction mixture, was A_0 (corresponding turnover number N_0). The activity decreased with time and reached a steady-state value A_{st} (turnover number N_{st}). The catalyst was then contacted with the gaseous mixture containg 0.4 ppm of C_4H_4S or 3 ppm H_2S (phase II or poisoning phase). The activity decreased to a steady-state level, A_{inf} which may or may not be equal to zero, called the thiotolerance level. Thio-resistance is linked to the rate of deactivation. The toxicity is defined as the number of metal atoms deactivated by one molecule of poison. After the phase II the samples were either decontaminated using the sulfur-free mixture or regenerated using flowing hydrogen. The third phase (phase III) was the decontamination phase using a mixture $H_2–C_6H_{12}$ without the S-containing compound. The activity reached a new steady-state (A_{decon}).

The effluents were analysed by gas chromatography after separation of the components using a Carbowax 20 M on Chromosorb W column (length 2 m, diameter 1.4 in) maintained at 353 K. The reaction rate was limited neither by thermodynamics nor by diffusion processes, provided conversion was lower than 10%. The sample weight was between 5 and 15 mg and the more active solid (Pt/Al_2O_3) was diluted in inactive α-Al_2O_3. The total flow rate of the reactants was 7.2 dm^3 h^{-1}.

Regenerations

After the phase II in the presence of thiophene or of H_2S (activity equal to A_{inf}) regenerations by sulfur removal were studied at various temperatures, between 543 and 673 K, under a flow of hydrogen (3.6 dm^3 h^{-1}) in the absence of air. The heating rate was 2 K min^{-1} and the regenerations were performed overnight. After cooling, the activity towards cyclohexane dehydrogenation under the sulfur-free mixture

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† 1 Torr = 133.322 Pa.

(A_{reg}) was then measured at 543 K and compared with the A_0 and A_{st} values.

Results

Physicochemical Characteristics

In Table 2 are reported the main characteristics of the solids, the sulfur and chlorine contents and the dispersion deduced from volumetric measurements.

The B.E.T. areas of the supports are not significantly changed by the preparation of the catalysts.

For the alumina-supported solids the particle sizes deduced from electron microscopy are in agreement with the values obtained by chemisorption. The mean particle size of the Pd/Al_2O_3 I solid is 3 nm and the repartition is narrow, all the particles having a diameter between 2.5 and 3.5 nm. The treatment at 1173 K (Pd/Al_2O_3 I′ solid) leads to the disappearance of the small particles; the distribution becomes broad with particles ranging between 30 and 60 nm.

For the silica–alumina-supported palladium solids, as the reduction temperature increases from 543 to 673 K the dispersion deduced by chemisorption decreases from 27 to 20%. The sulfate groups initially present on the support are reduced to hydrogen sulfide, poisoning the metal. In this case there is no agreement between the particle diameters deduced from chemisorption and from electron microscopy: 5.6 nm from H_2 chemisorption (dispersion 20%) and mean particle diameter of 4 nm from TEM measurements.

Catalytic Activities: Phases I, II, III

Phase I

In Table 3 are reported the catalytic activities expressed in turnover frequencies at zero time (N_0) and at the steady-state (N_{st}) as well as the percentage of deactivation during phase I. Note that N_0 is measured after 1 min on stream. The turnover numbers are calculated from the chemisorption measurements.

Alumina Support. With the Pd/Al_2O_3 solids, benzene is the only product and the deactivation remains moderate (Fig. 1). This deactivation is probably due to the deposition of carbon-containing species on the surface of the Pd particles. The initial turnover number lies within a limited range whatever the origin of the support, the nature of the precursor salt and the dispersion value (between 4 and 38%). It has been reported already that the dehydrogenation of cyclohexane is structure insensitive and that the rate is a measure of the free metal surface.[13–17]

The catalytic activity of the Pt/Al_2O_3 solid studied here agrees very well with the values reported in the literature.[13,16] Pt is much more active than Pd.

The initial activity of Rh is comparable to that of Pd but the deactivation is more pronounced. At the same time, benzene is no longer the only product; small amounts (<0.2% of the converted cyclohexane) of light hydrocarbons are observed.

Silica–Alumina Support. With the silica–alumina support the initial activity N_0 of Pd is clearly increased, whatever the reduction temperature. This activity increase in the presence of an acidic support has been noticed already for the hydrogenation of benzene[18–20] and toluene.[21] It was related either to an electron-deficient character of the metal surface atom or to the creation of new active centres at the Pd/support interface.

The initial turnover number increases with the reduction temperature in spite of the loss of accessible surface Pd atoms due to poisoning by sulfur coming from the support. This is in favour of the creation of new active Lewis acid centres on the acidic support, their number increasing with the reduction temperature.

For a given reduction temperature (673 K) the deactivation is more marked with the silica–alumina support than with alumina. However, the steady state is always obtained after 3 h on stream. Benzene is no longer the only product and some

Table 2 Physicochemical characteristics of the solids

solid	reduction temperature/K	sulfur [ppm (wt.)]	chlorine (wt.%)	noble-metal dispersion (%)
Pd/Al_2O_3 I	673	<19	0.3	38[a]
Pd/Al_2O_3 I′	673	—	—	4[b]
Pd/Al_2O_3 II	673	180	0.06	25
Pd/Al_2O_3 III	673	—	0.7	21
Pt/Al_2O_3	673	165	0.67	37
Rh/Al_2O_3	673	140	0.77	63
$Pd/SiO_2–Al_2O_3$	543	1200	0.21	27
$Pd/SiO_2–Al_2O_3$	673	—	—	20

—, not determined. Mean particle size determined by electron microscopy: [a] 3 nm; [b] between 30 and 60 nm.

Table 3 Catalytic activities expressed in turnover numbers during phase I

solid	N_0/s^{-1}	N_{st}/s^{-1}	deactivation (%)
Pd/Al_2O_3 I	1078	1030	4.4
Pd/Al_2O_3 I′	1150	1130	1.7
Pd/Al_2O_3 II	1250	1160	7.2
Pd/Al_2O_3 III	1100	1000	9.1
Pt/Al_2O_3	11500	10710	6.9
Rh/Al_2O_3	1170	910	22.2
$Pd/SiO_2–Al_2O_3$ (543)	3020	2720	9.9
$Pd/SiO_2–Al_2O_3$ (673)	3640	3030	16.7

Turnover numbers deduced from chemisorption measurements: N_0 after 1 min on stream, N_{st} at the steady state.

light hydrocarbons are observed. The deactivation increases with the reduction temperature. It is known than an acidic support favours deactivation by coking[22] and that the number of Lewis centres involved in this polymerisation process increases with the temperature of activation.

Phase II in Presence of Thiophene

In Figs. 2 and 3 the relative activity A_t/A_{st} (A_t activity at time *t* during the phase II, A_{st} steady-state activity during the phase I) is plotted *vs.* the number Λ of thiophene molecules per surface palladium atom. The values of the thio-tolerance expressed as A_{inf}/A_{st} are also reported in Table 4.

Pd/Al_2O_3. For the Pd/Al_2O_3 solids (Fig. 2) a drastic deactivation is observed leading to an inactive catalyst whatever the support, the precursor salt or the dispersion. The deactivation curves are identical for the three solids Pd/Al_2O_3 I, I′ and II prepared with $Pd(C_5H_7O_2)_2$. The sulfur or the chlorine present initially on the support and the dispersion (11–38%) have no effect on the thio-tolerance (residual activity) or on the thio-resistance (deactivation rate).

The thio-resistance is clearly improved in the presence of chlorine in the precursor (solid Pd/Al_2O_3 III) in contrast with the chlorine initially present on the support, probably because of a better proximity between Cl and Pd. Such an influence of chlorine has already been mentioned in the case of Pt for cyclohexane dehydrogenation[13,22] and of Pd for styrene and ethylbenzene hydrogenations.[23]

The initial toxicity given by the slope of the linear part of the curve for the zero time, assuming that the poison is well dispersed on the solid, is equal to one S per five Pd_s. A similar result has been reported already for Pt poisoning by thiophene during benzene hydrogenation[24] and cyclohexane dehydrogenation.[13] In the case of single crystals, one sulfur atom poisons four to five surface metal atoms.[25]

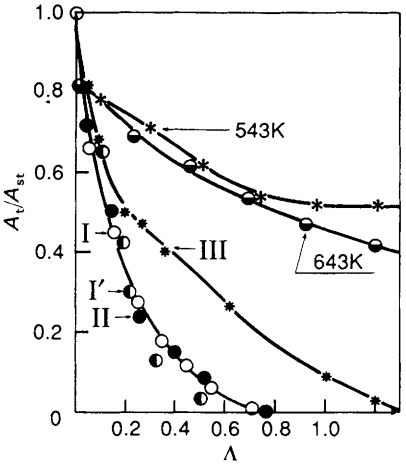

Fig. 2 Relative activities A_t/A_{st} during the phase II (mixture of C_6H_{12}, H_2 and C_4H_4S) *vs.* Λ. Λ = number of thiophene molecules per surface palladium atom for the palladium supported solids. Pd/Al_2O_3: solids I (◐), I′ (○), II (●) and III (✱) reduced at 673 K. Pd/SiO_2-Al_2O_3: solids reduced at 543 K (✱) and at 643 K (⊖)

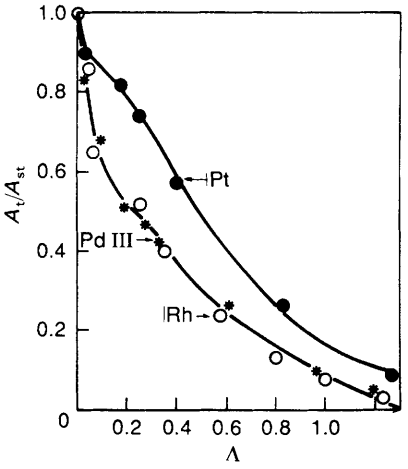

Fig. 3 Relative activities A_t/A_{st} during the phase II (in presence of C_4H_5S) *vs.* Λ: comparison between the three metals (Pd, Pt, Rh) supported on alumina. ✱, Pd/Al_2O_3 III; ●, Pt/Al_2O_3; ○, Rh/Al_2O_3

Pt/Al_2O_3 *and* Rh/Al_2O_3. The behaviour of the Rh/Al_2O_3 and Pt/Al_2O_3 solids prepared with chlorinated precursors is compared with that of the solid Pd/Al_2O_3 III (precursor H_2PdCl_4) (Fig. 3 and Table 4). Rhodium behaves as palladium: the deactivation is complete. In the presence of sulfur the amount of light hydrocarbons decreases in comparison with the amount observed in phase I.

The thio-tolerance of Pt is clearly higher than that of Pd and Rh; the A_{inf}/A_{st} value stabilizes to 12% (Table 4). This value is higher than that reported by El Azhar *et al.* (2%)[16] in the presence of 1.4 ppm of thiophene in the gaseous phase but is close to that reported by Barbier *et al.*[13] for a chlorine-free solid. In the latter study the thio-resistance is lower than the thio-resistance of our Pt/Al_2O_3 solid. As for Pd, the presence of chlorine in the precursor improves the thio-resistance. For an Ir/Al_2O_3 solid the thio-tolerance level has been found equal to 1% in the presence of 0.3 ppm of thiophene in the gaseous phase.[14,15,17]

With the alumina support, the thio-tolerance of the various metals increases in the following order: Pt ≫ Pd ≈ Rh ≈ Ir.

Pd/SiO_2-Al_2O_3. For the Pd/SiO_2-Al_2O_3 solid the initial toxicity is strong; the activity decreases by *ca.* 15% during the first 10 min on stream (Fig. 2 and 4). Afterwards the activity decreases only slowly with time. In fact the deactivation is limited and tends to stabilize to a value A_{inf} differing from

Table 4 Catalytic activities during the phase II (poisoning by thiophene) and phase III (decontamination after poisoning by thiophene)

solid	$(A_{inf}/A_{st}) \times 10^2$	$A_{decon}/A_{st} \times 10^2$ 300 min	 600 min
Pd/Al_2O_3 I	0	9	16
Pd/Al_2O_3 I′	0	18	21
Pd/Al_2O_3 II	0	13	—
Pd/Al_2O_3 III	0	9	13
Pt/Al_2O_3	12	63	66
Rh/Al_2O_3	0	14	20
Pd/SiO_2-Al_2O_3 (543)	51	120	*ca.* 140
Pd/SiO_2-Al_2O_3 (673)	42	135	*ca.* 140

— not determined.

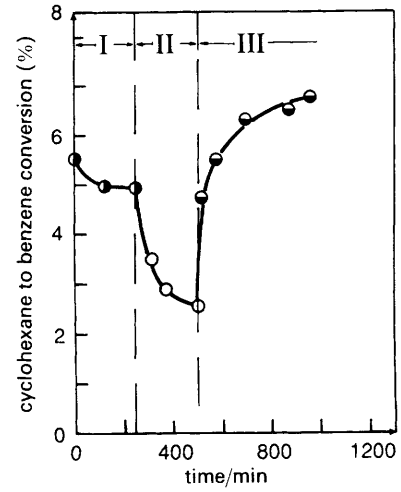

Fig. 4 Catalytic run for the solid Pd/SiO_2–Al_2O_3 reduced at 543 K. Catalytic activity was measured at 543 K as a function of time. Reactants: Cyclohexane, hydrogen. Presence of 0.4 ppm of thiophene in phase II. ◑, Phase I; ○, Phase II; ⊖, Phase III

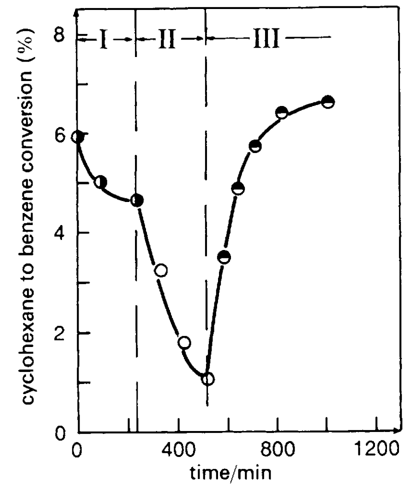

Fig. 5 Catalytic run for the solid Pd/SiO_2–Al_2O_3 reduced at 543 K. Catalytic activity was measured at 543 K as a function of time. Reactants: cyclohexane, hydrogen. Presence of 3 ppm of hydrogen sulfide in phase II. ◑, Phase I; ○, Phase II; ⊖, Phase III

zero after *ca.* 4 h. It has been verified that the value thus obtained (Table 4) is still observed after 24 h on stream. The reduction temperature (543 or 673 K) does not strongly affect the deactivation.

This better thio-tolerance is related to the acidity of the support. It is already known that the thio-tolerance of supported Pt or Ir in the dehydrogenation of cyclohexane increases when the metals are supported on acidic supports.[13–17] It is generally assumed that the metal particles are thus electron-deficient leading to the formation of less strong M—S bonds.

Phase III. Decontamination after Phase II in Presence of Thiophene

Upon contacting with the sulfur-free mixture at 543 K, the activities slowly increase with time. The relative recoveries observed during phase III are indicated in Table 4, after two times on stream: 300 and 600 min. The Pd/Al_2O_3 catalysts recover between 13 and 21% of their stabilized activity in phase I. There is no clear influence of the nature of the precursor or of the origin of the support on the decontamination. Such a low decontamination of Pd has been reported already during the hydrogenation of styrene at 353 K.[26] The behaviour of Rh is similar to that of Pd but the decontamination of Pt is much more important, as already noticed.[13]

When Pd is supported on SiO_2–Al_2O_3 the decontamination is very important (Fig. 4). Surprisingly, the activity A_{decon} reaches a value superior to the initial activity A_0 and to the steady-state activity A_{st}: the ratio A_{decon}/A_{st} reaches *ca.* 140%. Thio-tolerance and thio-decontamination have been related already to the concept of the electron-deficient character of small particles when supported on acidic carriers. The behaviour observed here will be discussed later. During the decontamination phase the activity towards hydrogenolysis is decreased in comparison with the same catalyst in phase I.

Use of H_2S *as Poisoning Molecule during Phase II*

The behaviour described above during phase II and phase III for the Pd/SiO_2–Al_2O_3 solid is similar when thiophene (0.4 ppm in the gaseous phase) is replaced by H_2S (3 ppm in the gaseous phase) (Fig. 5). During phase II the stronger deactivation observed in the presence of H_2S than in the presence of C_4H_4S is ascribed to the higher concentration of pollutant. During the decontamination phase after 300 min on stream the $(A_{decon}/A_{st}) \times 100$ value reaches *ca.* 125.

The thiophene molecule is transformed into H_2S and C_4H_{10} under the reaction conditions. Furthermore, the behaviour of the Pd/SiO_2–Al_2O_3 solid during the decontamination phase being uninfluenced by the nature of the poisoning molecule, H_2S or C_4H_4S, is not due to carbon or hydrocarbon molecules arising from C_4H_4S.

Regenerations by H_2

Pd/Al_2O_3. After phase II the solids were treated by H_2 at various temperatures between 543 and 673 K, the treatments being performed overnight. The activity at 543 K towards the sulfur-free mixture is then measured after 1 min on stream (A_{reg}). Fig. 6 shows the percentage of regeneration A_{reg}/A_{st} at various temperatures above 573 K for the Pd/Al_2O_3 I and I′ solids after poisoning in the presence of thiophene. The curves are identical. At 673 K the regeneration is complete. This conclusion is in opposition to the work of l'Argentiere and Figoli[26] but in this latter case the regenerations were performed between 393 and 513 K. Surprisingly the efficiency

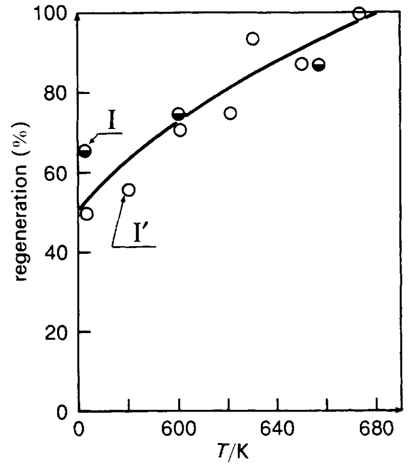

Fig. 6 Regenerations by H_2 at various tempertures for the solids Pd/Al_2O_3 I (⊖) and I′ (○) after poisoning in phase II in the presence of thiophene

of the regeneration by H_2 is greater for Pd/Al_2O_3 than for Pt/Al_2O_3 solids. According to the literature the regeneration of Pt is complete only at 1073 K and, at 773 K, irreversibly adsorbed sulfur correspond to *ca.* 0.4 S per Pt_s.[27,28] The Pd—S bond would be less stable than the Pt—S one. Note, however, that the thio-tolerance of Pd is lower than that of Pt and that the decontamination of Pd at 543 K by the sulfur-free mixture is more difficult than the decontamination of Pt.

$Pd/SiO_2-Al_2O_3$. The regeneration by hydrogen is very efficient for the $Pd/SiO_2-Al_2O_3$ solid. As during the decontamination process, the activity becomes higher than the A_0 and A_{st} activities measured during phase I. For instance, regeneration at 543 K overnight leads to a A_{reg}/A_{st} ratio of 140%. Let us recall the value of 140% for the A_{decon}/A_{st} ratio measured after 600 min of decontamination under the sulfur-free mixture.

Discussion and Conclusion

In this paper deactivation of supported palladium solids is studied during cyclohexane aromatization in the absence and in the presence of sulfur-containing molecules, hydrogen sulfide or thiophene. The same behaviour is observed whatever the sulfur compound, suggesting that thiophene is hydrogenated into H_2S and butane under the reaction conditions.

With an alumina support, in the absence of a sulfur-containing compound, platinum is a much more efficient catalyst than palladium and rhodium, since turnover numbers measured in phase I increase ten-fold going from Pd (or Rh) to Pt. The thio-tolerance of Pt/Al_2O_3 is also clearly higher than that of Pd/Al_2O_3 and Rh/Al_2O_3. In phase II, the activity of Pd falls to zero whatever the alumina support, the precursor salt and the dispersion. Nevertheless the thio-resistance of Pd is slightly improved by the use of a chlorinated precursor. The presence of sulfate- and/or chlorine-containing species in the alumina support does not change the catalytic behaviour.

The decontamination by the sulfur-free mixture at the temperature of the reaction (543 K) is less efficient for palladium and rhodium than for platinum. For instance after 600 min on stream decontamination levels of 13–21% and 66% are observed for the Pd/Al_2O_3 and Pt/Al_2O_3 solids, respectively. In contrast, the regeneration under pure hydrogen is easier for palladium than for platinum. The catalytic activity of Pd/Al_2O_3 is fully restored after hydrogen treatment at 673 K; under the same conditions the Pt/Al_2O_3 catalyst recovers only 50% of its initial activity. It may be postulated that the decontamination level is connected with the sulfur coverage and that the regeneration level is correlated with the strength of the metal–sulfur bond. The sulfur coverage is probably higher on Pd than on Pt but the Pd—S bond is less stable than the Pt—S one. Note that the free energy of formation of the bulk sulfides from the elements is less negative for Pd—S (-78 kJ mol^{-1}) than for Pt—S (-88 kJ mol^{-1}).[3]

The behaviour of Pd supported on silica–alumina differs strongly from that of Pd supported on alumina. With a sulfur-free mixture, during phase I, the deactivation is more pronounced for the $Pd/SiO_2-Al_2O_3$ solid (*ca.* 17%) than for the Pd/Al_2O_3 one (<7%). The acidic support favours deactivation by coking. Nevertheless, at the steady state the activity is higher with silica–alumina than with alumina: the turnover number N_{st} is close to 3000 s^{-1} and to 1000 s^{-1} for $Pd/SiO_2-Al_2O_3$ and Pd/Al_2O_3, respectively.

Such an activity increase for the dehydrogenation of cyclohexane has been encountered in the case of Pt supported on silica–alumina[16] but not in the case of Ir.[17] It might be assumed that benzene obtained on the metal particle migrates towards the acidic support leading to free metal sites to assume again the transformation of cyclohexane into benzene. By increasing the acidity of the support, for instance by increasing the temperature of reduction, the migration would be favoured.

The thio-tolerance is strongly increased when palladium is supported on $SiO_2-Al_2O_3$, as already seen for Pt and Ir.[13–17] This behaviour has been assigned to the electron-deficient character of the metal surface atoms in the presence of an acidic carrier; as a consequence the strength of the M—S bond is decreased.

The most surprising result of this work concerns the decontamination of the $Pd/SiO_2-Al_2O_3$ solid under a sulfur-free mixture at 543 K (phase III). Decontamination leads to an activity A_{decon} higher than the initial activity A_0 and of course than the steady-state activity A_{st} determined during phase I. The ratio A_{decon}/A_{st} can reach values as large as 1.4 and the ratio A_{decon}/A_0 values as large as *ca.* 1.2. Since such behaviour is independent the poisoning molecule, H_2S or C_4H_5S, this overactivity is not due to carbon or hydrocarbon molecules arising from C_4H_5S. Regeneration under pure hydrogen leads also to an activity A_{reg} superior to the activities A_0 and A_{st} measured during phase I. To our knowledge such a result has never been reported and seems to be characteristic of palladium. In the case of Pt[13,16,22] and of Ir[14,15,17] the decontamination is favoured by an acidic support but the activity does not reach the values measured in phase I. For instance, the ratio A_{decon}/A_{st} can reach 0.57 when Pt is supported on alumina and 0.71 when Pt is supported on silica–alumina.[16] With Ir these ratios are equal to *ca.* 0.2 and 0.5, respectively.[17]

Various explanations can be advanced to take into account the overactivity observed after decontamination and regeneration in the case of $Pd/SiO_2-Al_2O_3$. (i) Changes in the metal particle size could be at the origin of the increase in activity. In fact TEM and hydrogen chemisorption measurements show that the palladium dispersion is not modified during the various phases of the experiments. (ii) Sulfur could remove the carbon residues previously deposited at the surface of the palladium particles.

The deactivation observed during phase I is due to the formation of carbon deposits at the surface of the palladium particles, this deactivation being more severe with an acidic support. The deactivation observed during phase II is mainly due to sulfur poisoning of the metallic phase. During the decontamination step (phase III) adsorbed sulfur would be progressively removed by the cyclohexane–hydrogen mixture. From literature data[1,29,30,31] it is known that the presence of sulfur inhibits the formation of carbon residues since this formation requires an ensemble of several atoms. So carbon residues are not formed during phase III. But in our case, as the activity after decontamination exceeds the activity at the steady state in phase I, it is necessary to consider that some carbon residues are removed either in phase II or in phase III. The adsorbed sulfur is expected to increase the reactivity of carbon deposits towards hydrogen. From pulse experiments we have verified that there is a coverage of the metallic surface by the carbon in the very first moments of the reaction. The initial activity A_0 here reported and determined after 1 min on stream differs from *ca.* 30 to 40% of the 'true' initial activity. So in fact the activities after decontamination (A_{decon}) and after regeneration (A_{reg}) are superior to the activity at the steady state (A_{st}), but do not exceed the initial activity.

(iii) A promoting effect of sulfur could be considered, the sulfur compound blocking some sites but creating particular sites. In a forthcoming paper we will show, from IR experiments, that, after decontamination at 543 K or after regeneration under pure H_2 at 673 K, some small amounts of sulfur remain adsorbed on the metal particles, whatever the support, alumina or silica–alumina. However, the initial activity can be totally restored. So the possibility of a promoting effect of sulfur in the case of palladium will be discussed.

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