

Compared properties of Pd on thermo-conductor supports (SiC, Si₃N₄) and Pd on oxide supports (Al₂O₃, SiO₂) for the 1,3-butadiene hydrogenation reaction

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Abstract

Palladium catalysts were prepared by impregnation with Pd(II)-bis-acetylacetonate dissolved in toluene on various nonporous supports having very different thermal properties, SiO₂, Al₂O₃, Si₃N₄, and SiC, and their catalytic properties were tested for the gas-phase 1,3-butadiene hydrogenation reaction. The mean metal particle size of 0.5 Pd wt% loaded catalysts was similar (4 nm) for all supports. However, Pd particles have different Pd_{3d5/2} XPS-binding energies, a sign of different electronic properties through their metal-support interactions. All catalysts show a decrease of their activity versus time at the beginning of a reaction run. However, the effect is more or less pronounced on the different catalysts. The activity of the Pd/SiO₂ and Pd/Si₃N₄ catalysts decreased rather rapidly until a stable situation was reached. This is not the case for Pd/Al₂O₃ and Pd/SiC catalysts whose activity decreased continuously with time even after 20-h working. No direct relationship can be drawn between the thermal conductivity of the support and the deactivation process. The deactivation via thermal effects induced on the metal particles by the hydrogenation reaction (exothermic and working with a very high TOF) is consequently not the predominant one. The evolution observed is in fact the consequence of the stabilization of the catalyst, probably via the formation of carbonaceous residues, which actually depend on the intrinsic properties of the metal/support couple.

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1. Introduction

Partial hydrogenation of dienes and alkynes is of great industrial importance [1,2]. Butadiene is present as an impurity in C₄ alkenes produced by steam cracking and its content must be considerably reduced in butadiene-butene mixtures. This is actually performed by selective hydrogenation of butadiene. A good process will consequently work in such a way that the complete hydrogenation of butadiene into butenes will be effective until the complete conversion of the diene is reached, i.e., avoiding any formation of the completely hydrogenated (butane) molecule. For these reactions, Pd is still considered as the best catalyst. However, it has been shown that its activity and selectivity can be strongly influenced by the metal dispersion, the nature of the support, and the preparation method [3–5]. Moreover, such a reaction

is sensitive to the surface structure; the hydrogenation rate has been found to be about five times more rapid with the more open (110) Pd face than with the close-packed (111) surface [6]. Both single-crystal surfaces were found to have a constant activity versus time and a selectivity into butenes close to one up to the quasi-complete conversion of butadiene. This is not the case for gas-phase hydrogenation of butadiene on supported Pd catalysts, which seems to depend on the nature of the support. While only a slight decrease of the initial activity has been observed for Pd on alumina [7], a rapid decrease of activity was observed versus time at the beginning of the reaction run for Pd on silica, before stabilization [6]. It is frequently postulated that poisoning, which actually occurs at the beginning of the reaction, is associated with the formation of carbonaceous residues. The presence of carbonaceous residues could also influence the selectivity toward butenes; it has been proposed that they would favor the *n*-butane formation [8] or, on the contrary, could either block the sites responsible for the further/total hydrogenation of butenes as the reaction proceeds or create the sites re-

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quired for selective formation of butenes (via carbonaceous overlayers) [9]. The carbonaceous residues may also depend on the acidic properties of the support and modify the activity/selectivity, and their variation with time under stream, for the considered reaction [10].

In order to improve the selectivity of competitive hydrogenation, Pd-based bimetallic catalysts were often employed [1,11–14]. The actual influence of the second metal added to Pd is not clearly established, and many explanations have been tentatively proposed. One can invoke a possible electronic influence, a structural promotion, and/or a location at specific sites of the added metal.

The modification of the activity/selectivity versus time can be due to a poisoning of some specific sites having an overactivity, such as the low-coordinated sites present at edges and corners of the Pd particles. In that sense the location of a nonreactive element especially at the edges and the corners, like Cu in PdCu [15], can be a way to limit the poisoning.

Moreover, one must keep in mind the high exothermicity of the reaction which, combined with the very high turnover number of palladium surface atoms, could cause problems in heat transfer and local increase of the temperature of the active Pd particles. One way to avoid these problems is the use of highly thermo-conducting materials as support of the Pd catalyst. Of these, silicon carbide and, to a lesser extent, silicon nitride are among the most highly thermo-conducting compounds, on which it is possible to deposit palladium as fine particles by chemical means [16,17]. Moreover, on silicon nitride Pd undergoes a peculiar electronic interaction which can modify its catalytic properties [17].

In the present paper we will compare the catalytic properties of the gas-phase hydrogenation of 1,3-butadiene of Pd deposited on supports showing very different thermo-conductivity, SiC, Si₃N₄, and Al₂O₃, and SiO₂ which has the lowest thermal properties.

2. Experimental

2.1. Supports and catalyst preparation

Nonporous materials in the shape of powders with similar BET specific surface areas were used as supports of the active Pd metallic phase. The main characteristics of these powdered supports are given in Table 1. The SiC support, from Nippon Carbide, presents the low temperature cubic β phase [16]. The silicon nitride support, from Goodfellow, was mainly constituted by the low temperature hexagonal α phase; the presence of some high temperature β phase was also measured by XRD [17]. More classical nonporous α -alumina and amorphous silica supports, produced by Rhône-Poulenc, were used for comparison. Known values of the thermal conductivity of such compounds are reported in Table 1 for information.

Table 1
Main characteristics of the supports and of the Pd deposits

	β -SiC	α -Si ₃ N ₄	α -Al ₂ O ₃	SiO ₂
Density (g cm ⁻³)	3.2	3.2	4	2.2
BET specific surface area (m ² /g)	17	7	11	37
Intrinsic values ^a	540	105–225 [18]	32–35	6–11
Thermal conductivity at RT (W/m/K)				
For materials ^b	270	150	30	≈ 1

^a May vary a few with the crystalline phase and the crystallographic axis considered.

^b These are approximate values, which depend upon the manufacturing process. The reported values are among the highest given in the literature.

Catalysts were prepared by impregnation of the as-supplied supports with an adequate amount of Pd(II)-bis-acetylacetonate [Pd(C₅H₇O₂)₂] (99% from Strem) dissolved in toluene. After evaporation of the solvent and drying at 80 °C, the catalyst precursor was decomposed under argon flow at 773 K for 2 h, the increasing rate of temperature being limited to 1 K s⁻¹, and cooled to RT under this neutral atmosphere. It is then calcinated for 2 h at 623 K under oxygen flow (increasing rate of temperature of 1 K min⁻¹) and further reduced under hydrogen flow for 2 h at 773 K (heating rate = 1 K min⁻¹). Finally, the reduced catalysts were flowed half an hour under Ar after cooling at RT.

2.2. Catalyst characterization

Induced coupled plasma (ICP) chemical analysis was used to determine the metal loading of the different catalysts. The samples were put in acid solution and heated. The acids solutions used were either H₂SO₄/HNO₃/HF at 523 K or HF + $\frac{2}{3}$ HCl/ $\frac{1}{3}$ HNO₃ at 423–473 K. The acid attack does not dissolve completely the silicon nitride, and silicon carbide and gray residues were observed. Alumina and silica were completely dissolved. The solutions were filtered before analysis by optical ICP in a Spectro monochromatic spectrophotometer (Pd wavelength was 340.6 nm).

The crystal structure of the supports was controlled by X-ray diffraction using a Bruker D5005 powder goniometer (type θ – θ) where the sample is fixed and the X-ray tube (Cu-K $_{\alpha 1+\alpha 2}$, $\lambda = 0.154184$ nm) and the detector rotate. Spectra were acquired in a 2θ range of 3–80° using 0.020° steps and an acquisition time of 1 s/step.

The catalysts morphology (size and distribution of the Pd particles supported on the powders) was determined by transmission electron microscopy (TEM). The microscope is a JEOL JEM 2010, operating at 200 kV, equipped with a LaB₆ tip, a high-resolution pole piece, and a Pentafet-LinK ISIS EDS-X spectrometer (Oxford Instruments). High-resolution electron microscopy (HRTEM) allows lattice imaging of the palladium particles and of the support. Chemical analysis (from several hundreds of nanometers down to 3-nm regions) was achieved by energy-dispersive X-ray spectroscopy (EDS-X) in the TEM in order to check

the local composition as well as the absence of pollutants. Size distributions were obtained from TEM micrographs; the mean size of the particles (d_{Pd}) is determined using the formula d_{Pd} (nm) = $\sum n_i d_i / \sum n_i$, where n_i is the number of particles corresponding to a diameter d_i (nm).

Photoemission measurements (XPS) were performed using an Escalab 200R from Fisons Instruments. Some charge effect can appear during measurements; all data are corrected taking the XPS-binding energy (BE) of respectively the Si_{2p} level of SiC at 100.2 eV, the N_{1s} level of Si₃N₄ at 397.6 eV, the Al_{2p} level of Al₂O₃ at 74.2 eV, and the Si_{2p} level of SiO₂ at 103.4 eV, as reference energy [19]. For quantitative analysis, the areas of the peaks considered are corrected by taking into account their respective cross sections, the spectrometer transmission (varying as the reciprocal of the square root of the kinetic energy of the photoelectrons (KE^{-0.5}) in the energy region considered), and the mean free path of electrons (taken as proportional to the kinetic energy of the photoelectrons (KE) in the energy region considered).

2.3. Catalytic measurements

The 1,3-butadiene hydrogenation was carried out primarily between 273 and 313 K in a flow reactor at atmospheric pressure. The reaction was performed in excess of hydrogen (H₂/HC = 6.65), the reactive mixture being diluted in He (He/(H₂ + HC) = 6.5). The relative flows were set with Brooks flow gauges; the total flow was fixed at 10 l h⁻¹. Products analysis was performed by gas chromatography. The selectivity into butenes is defined by $S_1 = P_{\text{butenes}} / \sum (P_{\text{butenes}} + P_{\text{butane}})$; the relative amount of 1-butene in the butenes cut is measured by $S_2 = P_{1\text{-butene}} / \sum (P_{\text{butenes}})$. For the TOF determination, the dispersion D is calculated following the expression $D = 1.1/d$ (d being the mean size diameter, expressed in nm), valid for fcc Pd particles [20].

For easier heat transfer between the thermostated bath (which fixes the reaction temperature) and the catalyst, reactors consisting of stainless-steel tubes of $\frac{1}{4}/\frac{1}{6}$ -inch outer/inner diameter (instead of quartz as usually) were used. Five milligrams of catalyst was blended with 45 mg of the inert support before introduction in the reactor.

As-prepared catalysts were retreated in the reactor for 2 h at 773 K in flowing O₂ and then reduced in H₂ for 1.5 h at 623 K. They were cooled under an He flow before the catalytic studies.

3. Results

The amorphous nature of the silica support was confirmed by X-ray diffraction. The alumina and silicon carbide supports exhibited respectively the known hexagonal α structure and the cubic β structure. For the silicon nitride support, the presence of some β phase was detected amid the hexagonal α phase.

Chemical analysis showed that for all the studied catalysts the Pd wt% is nearby 0.5%, which implies some loss of Pd during the whole preparation process. In fact, whatever the metal content and the support the loss was constant and around 0.15 wt%.

For such a low loading, the diffraction lines corresponding to the Pd metal were not detected in the X-ray diffractometers of the metalized catalysts.

Representative TEM micrographs of the studied catalysts are given in Fig. 1. The size distributions are reported as inserts in the TEM micrographs. The mean size of the Pd particles is close to 4 nm whatever the support (see Table 2).

XPS experiments showed differences in the Pd_{3d}-binding energies, which depend on the nature of the support. The Pd_{3d5/2}-binding energy is a little less than 335 eV on SiC and SiO₂. For Pd on Si₃N₄, it is nearly 1 eV more. The Pd_{3d5/2} BE on alumina ranges between these two values. For comparison, we measured a value of 335.3 eV for massive Pd using the same instrumental setup [21].

The measured values of the Pd loading, of the particle sizes, and of the XPS-binding energies for the different catalysts are given in Table 2.

In Figs. 2–5 are reported the conversion and the S_1 selectivity into butenes versus time for the studied catalysts, for experiments performed at 293 K. The general trend is a decrease of activity with time accompanied with an increase of the S_1 selectivity. However, these effects are more or less rapid and more or less pronounced on the various catalysts. For Pd on SiO₂ the initial decrease of the activity is important but the catalyst reaches a steady state after 5–6 h working; its activity is quite low in comparison with the others. The same tendency is observed for the Pd/Si₃N₄ catalyst, but with a higher steady-state activity. Pd on alumina and Pd on silicon carbide both present a higher activity and a less important decrease of activity with time. However, they have a lower S_1 selectivity. In Table 3 are given the turn over frequency (TOF), the S_1 selectivity (into butenes), and the S_2 selectivity (which measures the 1-butene ratio in the butenes cut) versus temperature.

The values of the activation energies for the considered reaction (butadiene → butenes) on the different catalysts reported hereafter correspond to calculations by taking into account sufficiently high activities to get a precise value, but only at temperatures so that the selectivity into butenes S_1 remains very high (above 85%), i.e., avoiding the 273 K value for the less active catalyst (Pd on SiO₂) and the values obtained at 303 K and above for the more active Pd/Si₃N₄ and Pd/SiC catalysts. The activation energy is 77 ± 2 kJ mol⁻¹ for Pd supported on SiO₂, Si₃N₄, and SiC. Taking into account the experimental values reported in Table 3 for the Pd/Al₂O₃ catalyst, a value significantly lower for the activation energy of the reaction is found (46 kJ mol⁻¹).

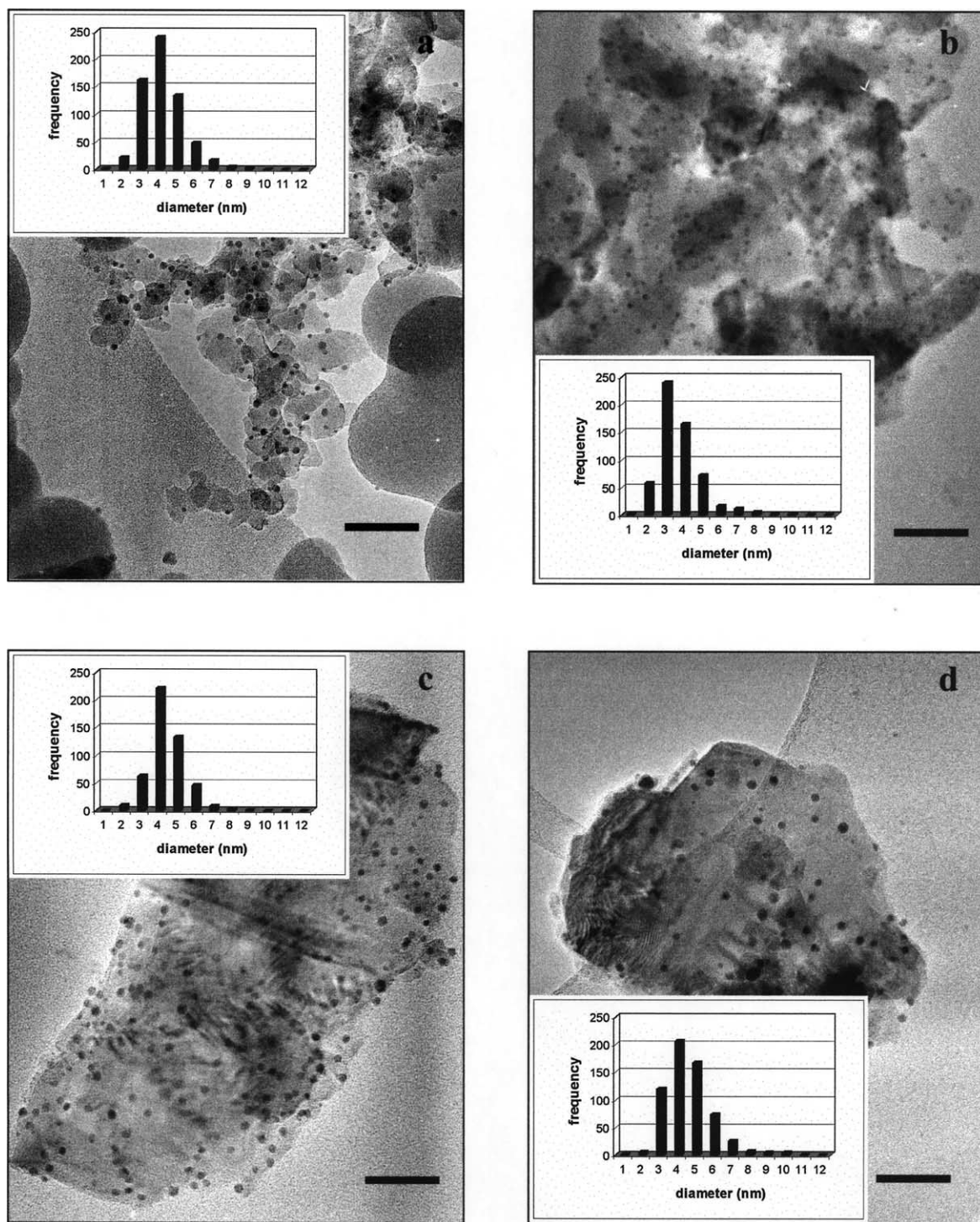


Fig. 1. Transmission electron micrographs of the four catalysts (scale bars are 100 nm). (a) Pd/SiO₂, (b) Pd/Al₂O₃, (c) Pd/Si₃N₄, (d) Pd/SiC. The size histograms are inserted in the respective micrographs.

4. Discussion

Let us first discuss the deactivation process observed at the beginning of the reaction runs performed at 293 K. The conversion decreases regularly with time under reaction with the Pd/SiO₂ catalyst and then stabilizes after some hours working, as observed earlier [6]. The behavior of the

Pd/Si₃N₄ catalyst is about the same. The evolution of the reaction versus time is different on the Pd/Al₂O₃ and Pd/SiC catalysts, for which the loss of activity is less important, but for which we never observed a complete stabilization. No correlation can be found between the thermal conductivity of the support (SiC > Si₃N₄ > Al₂O₃ > SiO₂) and the deactivation process during the reaction run. One can therefore

Table 2
Physico-chemical properties of the Pd-supported catalysts

	Pd/ β -SiC	Pd/ α -Si ₃ N ₄	Pd/ α -Al ₂ O ₃	Pd/SiO ₂
Pd loading (wt%)	0.61	0.48	0.54	0.52
TEM mean particle size (nm)	4.5	4.3	3.7	4.1
Dispersion D^a	0.24	0.26	0.3	0.27
Pd _{3d5/2} -binding energy (eV)	334.7	335.9	335.4	334.9

^a The dispersion, for Pd particles, is calculated following the relationship: $D = 1.1/d$; d being the mean diameter expressed in nm [20].

conclude that the heat transfer from the reacting metal particles to the support is not one of the main parameters for preventing the deactivation processes. This points out that the use of highly thermo-conducting materials, such as SiC, and Si₃N₄, for such an exothermic reaction working with a high TOF (i.e., liberating many calories per unit time) does not avoid the deactivation process.

One can therefore think that the main process appearing at the beginning of the considered reaction is its stabilization through the formation of carbonaceous deposits [10,13,22]. Looking at the activity/selectivity versus time curves measured at RT for Pd on SiO₂ and Si₃N₄ (Figs. 2 and 4), more precisely by considering the simultaneous decrease of activity and increase of selectivity into butenes to reach a 100% selectivity as soon as the catalyst exhibits a stable activity, one can propose a scenario in which the catalytically active sites responsible for the further total hydrogenation of 1-butene would be selectively blocked by these carbonaceous deposits or that the sites required for selective formation of the butenes are created as proposed by Crabb and Marshall [9]. Such a proposal is in contradiction with some conclusions of other authors who propose that the carbonaceous residues at the surface would make the catalyst less selective into butenes [23]. Looking again at Figs. 2–5, one sees clearly that the stabilization process is more or less rapid depending on the support; moreover, the Pd/Al₂O₃ catalyst

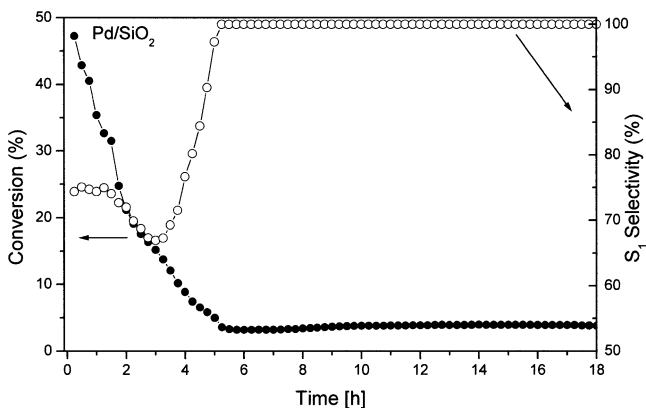


Fig. 2. 1,3-Butadiene conversion (%) and selectivity $S_1 = P_{\text{butenes}} / \sum(P_{\text{butenes}} + P_{\text{butane}})$ (%) for the Pd/SiO₂ catalyst. Flow rates: H₂ = 1.33 h⁻¹, butadiene = 0.2 h⁻¹, and helium = 9 h⁻¹; temperature = 293 K.

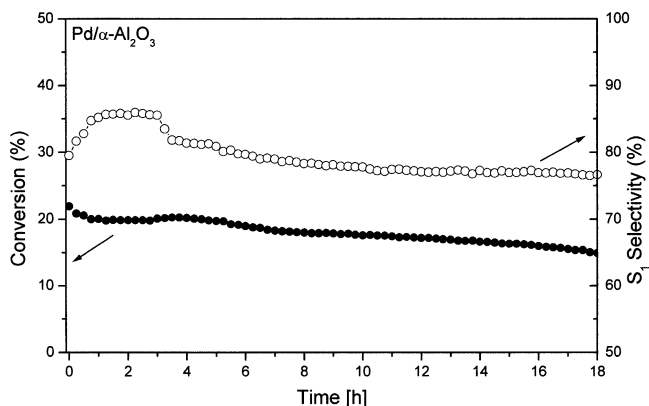


Fig. 3. 1,3-Butadiene conversion (%) and selectivity $S_1 = P_{\text{butenes}} / \sum(P_{\text{butenes}} + P_{\text{butane}})$ (%) for the Pd/Al₂O₃ catalyst. Flow rates: H₂ = 1.33 h⁻¹, butadiene = 0.2 h⁻¹, and helium = 9 h⁻¹; temperature = 293 K.

shows a quite different behavior since both the activity and the S_1 selectivity decrease simultaneously with time. Such behavior has also been observed on Pt catalysts and depends upon the acidity of the support [10].

In any case, the experimental values of activity/selectivity measured at different temperatures after 18-h working (Table 3) provide evidence that the S_1 selectivity rapidly decreases as soon as the conversion becomes higher than about 15%. This is a sign that the active sites for further hydrogenation are in fact always present; and that the thermodynamic and kinetic parameters simply govern the reaction on a stabilized surface.

Let us now consider the reaction with respect to the intrinsic properties of the Pd particles. All the studied catalyst have about the same characteristics with respect to the metal loading ($\approx 0.5\%$) and the mean size (≈ 4 nm). Whatever the sample, the line shape of both the Pd_(3d5/2+3d1/2) XPS peaks and the corresponding M_{4,5}VV Auger spectrum is quite comparable to that obtained for a reduced Pd⁰ state as measured for a clean and massive palladium sample, and not to an oxidized Pd²⁺ state as measured for PdO [21]. Never-

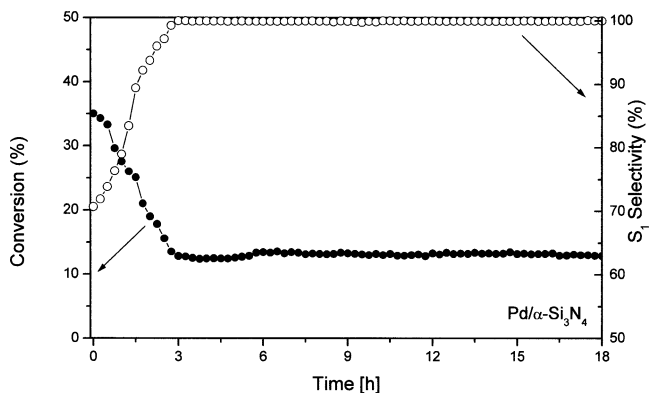


Fig. 4. 1,3-Butadiene conversion (%) and selectivity $S_1 = P_{\text{butenes}} / \sum(P_{\text{butenes}} + P_{\text{butane}})$ (%) for the Pd/Si₃N₄ catalyst. Flow rates: H₂ = 1.33 h⁻¹, butadiene = 0.2 h⁻¹, and helium = 9 h⁻¹; temperature = 293 K.

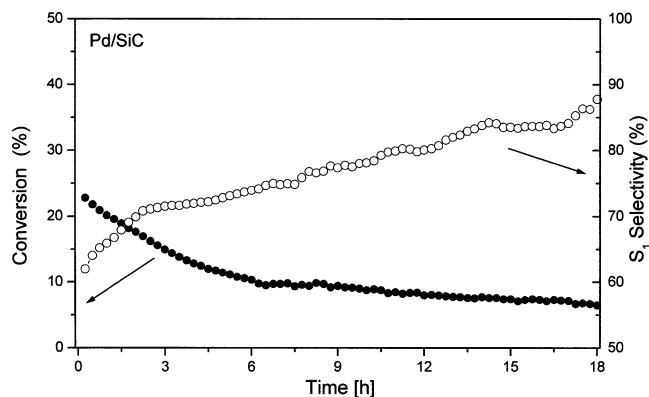


Fig. 5. 1,3-Butadiene conversion (%) and selectivity $S_1 = P_{\text{butenes}} / \sum(P_{\text{butenes}} + P_{\text{butane}})$ (%) for the Pd/SiC catalyst. Flow rates: $H_2 = 1.33 \text{ l h}^{-1}$, butadiene = 0.2 l h^{-1} , and helium = 9 l h^{-1} ; temperature = 293 K.

theless, the different values of the $Pd_{3d5/2}$ -binding energies for the different catalysts (see Table 2) can be considered as a sign of some modification of the electronic properties of the Pd particles induced by more or less support interaction. Simply, one can consider that Pd is in a neutral state on SiO_2 and on SiC, but somewhat electron deficient on Si_3N_4 ; Pd on Al_2O_3 shows an intermediate behavior. No direct correlation between the different parameters for the considered reaction (activity/selectivity/activation energy) and the $Pd_{3d5/2}$ XPS-binding energies of Pd emerges from the data collected on the different catalysts.

Table 3

Turnover frequencies (TOF in s^{-1}), $S_1 = P_{\text{butenes}} / \sum(P_{\text{butenes}} + P_{\text{butane}})$ and $S_2 = P_{1\text{-butene}} / \sum(P_{\text{butenes}})$ selectivities between 273 and 313 K for the studied catalysts under the experimental conditions used ($H_2/HC = 6.65$, $He/(H_2/HC) = 6.5$ and a total flow rate = 10 l h^{-1})

	T (°K)	% conversion	TOF (s^{-1})	S_1 (%)	S_2 (%)
Pd/ SiO_2	273	~0.4	~0.15	100	69
	283	1.15	0.41	100	68
	293	3.9	1.4	100	66
	303	10.4	3.5	100	65
	313	26	8.5	73	52
Pd/ Al_2O_3	273	4	1.2	96	58
	283	8	2.5	77	41
	293	14	4.5	76	47
	303	31	9.7	50	28
	313	37	10.5	45	26
Pd/ Si_3N_4	273	1.2	0.45	100	72
	283	3.5	1.4	100	71
	293	13	5	100	73
	303	44	16.5	65	26
	313	46	16.5	56	24
Pd/SiC	273	~0.6	~0.2	100	72
	283	1.7	0.55	100	72
	293	6.5	2	85	51
	303	13	4.2	67	44
	313	20.5	6.5	57	35

The values are reported for measurements made after more than 18 h on stream at 293 K.

The activation energy E^* is quite the same for Pd on SiO_2 , Si_3N_4 , and SiC, while the BE values are markedly different. E^* is lower only for Pd/ Al_2O_3 , whose BE value is in a range in between those of the others. However, the E^* value corresponds then not only to the butadiene \rightarrow butenes hydrogenation reaction but also to the consecutive transformation of butenes, well evidenced by the far from 100% S_1 selectivity.

Among the catalysts exhibiting a high S_1 selectivity after stabilization at 293 K (Pd on SiO_2 , Si_3N_4 , and to a less extent SiC) the Pd/ Si_3N_4 catalyst, which exhibits the higher $Pd_{3d5/2}$ BE value, has the higher activity. The 5 s^{-1} TOF (at 293 K and for a hydrogen pressure of 95 torr) is high and comparable to that measured on Pd single crystals for the same hydrogen pressure [6].

With respect to the selectivity into butenes, Pd/ Si_3N_4 appears also to be one of the more efficient, together with the Pd/ SiO_2 catalyst. Nevertheless, the performance of such a catalyst with respect to the selectivity into butenes remains quite bad; indeed, the formation of the completely hydrogenated product, the butane, is effective as soon as the conversion becomes higher than about 15%. In any case, the S_1 selectivity into butenes never reaches 100% for Pd/SiC and for Pd/ Al_2O_3 , even for very low conversion. Whatever the catalyst, the 1-butene represents about 2/3 of the whole amount of butenes as long as the selectivity remains close to 100%. This seems to be a general trend for “normal” palladium [7,22]. The *trans/cis* ratio in the 2-butenes is then close to 9, a quite high value often found on pure Pd [24] and interpreted in terms of butadiene adsorbed in two π -allylic states which would be mainly governed by the time-averaged conformational behavior of butadiene molecules in the gas phase, i.e., an *anti/syn* value of about 20/1 [25,26]. As soon as butane appears as a product of the reaction, the proportion of 2-butenes increases. This is the consequence of both the largely more rapid hydrogenation rate for the 1-butene as compared to 2-butenes and the rapid isomerization of 1-butene into the thermodynamically more stable 2-butenes.

5. Summary and conclusions

The preparation of Pd (0.5 wt%) catalysts by impregnation with Pd(II)-bis-acetylacetonate dissolved in toluene leads to the formation of metal particles having a very narrow size distribution centered near 4 nm whatever the (non-porous) support: SiO_2 , Al_2O_3 , Si_3N_4 , and SiC. Nevertheless, the XPS $Pd_{3d5/2}$ -binding energy depends on the support: it is quite high for Pd/ Si_3N_4 (nearby 336 eV). This is 1 eV higher than for Pd/ SiO_2 and Pd/SiC. Pd/ Al_2O_3 shows an intermediate binding energy value for the Pd XPS peaks.

Whatever the catalyst a decrease of the catalytic activity is observed versus time for the gas-phase hydrogenation of 1,3-butadiene. It is rapid and well pronounced, for both Pd/ SiO_2 and Pd/ Si_3N_4 catalysts, i.e., for Pd on supports having very different thermal properties. The behavior of Pd

supported on Al₂O₃ and on SiC, the most highly thermo-conducting support, is more complex and the length of time necessary for reaching a stable regime is much longer. In any case, no direct relationship can be drawn between the thermal conductivity of the support and the deactivation process. One can therefore conclude that the deactivation via thermal effects induced on the metal particles by the hydrogenation reaction (exothermic and working with a very high TOF) is not the predominant one. The evolution observed is in fact the consequence of the stabilization of the catalyst, probably via the formation of carbonaceous residues, which is actually dependent on the intrinsic properties of the metal/support.

Considering the stabilized catalysts, the Pd/Si₃N₄ catalyst (for which the Pd_{3d_{5/2}} XPS-binding energy is higher compared to the others and to massive palladium) can be considered slightly more efficient than the others; it shows a higher TOF and a good selectivity into butenes up to a slightly higher conversion.

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