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Palladium–alumina catalysts: precursor, support and dispersion effects in selective hydrogenation

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Summary — Palladium–alumina catalysts are prepared from various precursors and by different preparation methods. The metal fraction exposed (MFE) is estimated from CO chemisorption measurements and compared with electron microscopy observations. Infrared absorbance measurements allow estimation of the CO uptake by the carrier and show that the presence of Pd induces no significant increase in this uptake. The turnover frequency (TOF) in hydrogenation of but-1-yne decreases sharply when the MFE increases. This behavior is ascribed to the *intrinsic* electron-deficient character of the small particles, which can itself be influenced by metal–support interactions. These interactions also appear to be responsible for the long prestationary periods observed.

palladium-alumina catalyst / carrier effect / but-1-yne / hydrogenation / CO adsorption / infrared spectroscopy

Résumé — Catalyseurs palladium-alumine: influence du précurseur, du support et de la dispersion du métal en hydrogénation sélective. *Des catalyseurs palladium-alumine sont élaborés à partir de précurseurs et de modes de préparation différents. La fraction métallique exposée (FME) est évaluée d'après des mesures de chimisorption de CO et comparée aux observations effectuées en microscopie électronique. Des mesures d'absorbance dans l'infrarouge permettent d'accéder aux quantités de CO fixées par le support et montrent que la présence du palladium n'entraîne pas d'augmentation significative de ces quantités. La fréquence de rotation dans l'hydrogénation du but-1-yne diminue de façon marquée quand la FME augmente. Ce comportement est attribué à la déficience intrinsèque en électrons des petites particules, laquelle peut être modifiée par leurs interactions avec le support. Ces interactions semblent également responsables des longues périodes préstationnaires observées.*

catalyseur palladium-alumine / effet de support / but-1-yne / hydrogénation / adsorption de CO / spectroscopie infrarouge

Introduction

Activity and selectivity of palladium catalysts in the semihydrogenation of acetylenic compounds have been the subject of many studies [1, 2]. In the case of alumina-supported palladium, the influence of the metal dispersion in the hydrogenation of but-1-yne was examined previously in the liquid phase at high pressure (2 MPa) and the turnover frequency was shown to decrease sharply when the metal fraction exposed (MFE) increased [3]. A similar trend was observed in the gas-phase reaction at atmospheric pressure over two samples prepared in the same way [4]. In both cases, the role of *electron-deficient palladium* in highly dispersed Pd catalysts was invoked and this point was emphasized in a well-documented review [5]. However, the role of the carrier and the influence of the precursor require further investigations. The aim of the present work is to focus on such factors, taking into account detailed studies concerning the preparation of these palladium catalysts, their characterization by UV-visible diffuse reflectance spectroscopy [6], electron paramagnetic resonance and infrared spectroscopy of adsorbed CO [7].

Experimental section

Materials

Two types of alumina supports were used: a non-porous γ-alumina from Degussa (100 m^2/g) and a porous (Vp = 0.56 cm^3/g) η-alumina from Rhône-Poulenc (250 m^2/g). A non-porous silica carrier (Aerosil 200 from Degussa) was occasionally employed. Palladium compounds were supplied by Engelhard, France. All gaseous products were purchased from l'Air Liquide.

Preparation of catalysts

The catalysts were prepared from various precursors and by different preparation methods: (i) capillary impregnation by aqueous solutions of $PdCl_4^{2-}$ or $Pd(NO_3)_2$; (ii) competitive

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* Correspondence and reprints

exchange of $PdCl_4^{2-}$ and Cl^-; and (iii) anchoring of palladium acetylacetonate from a benzene solution. After drying, the samples were calcined in flowing oxygen at Tox = 673 K for 12 h, flushed by nitrogen at 293 K for 10 min, reduced in flowing hydrogen for 2 h at a fixed temperature Tr (373–773 K), and finally evacuated at Tr for 2 h before CO adsorption and infrared experiments; more details are given in reference [7]. For catalytic measurements, the activation procedure was the same except that the final evacuation was replaced by cooling in hydrogen down to the reaction temperature.

Techniques

CO chemisorption measurements were carried out at 293 K in a conventional static apparatus using a pressure sensor (Barocel type 590 from Datametrics). Some comparison experiments were performed with hydrogen at 373 K under $p \leqslant 100$ Torr (1 Torr = 101325/760 Pa) to avoid hydride formation [8]. The samples were also examined by transmission electron microscopy (TEM) on a JEOL JEM 100 CX II equipment.

The catalytic tests were carried out in a microreactor operating under differential conditions at atmospheric pressure in the 273–298 K range, with $pH_2/p_{butyne} = 5.5$. To avoid overheating, the sample was carefully mixed with carborundum (5–20 mg catalyst into 500 mg) and the activation procedure (see above) performed in situ just before the test. The palladium content of the catalysts was measured by inductively coupled plama emission spectroscopy (CNRS Laboratory, Vernaison, France).

Results and discussion

Determination of the metal fraction exposed (MFE)

- *Choosing CO as a dispersion probe. Determination of the amount adsorbed by the carrier*

The determination of the metal fraction exposed (MFE) by chemisorption measurements on Pd catalysts requires consideration of the following points. First when using H_2 as a probe molecule, the hydride formation may be avoided by using a definite procedure [8]; however, additional H_2 consumption due to hydrogen spillover [9] can induce uncertainties, especially in the case of reducible carriers.

Second if the probe molecule is CO, the first point is the CO/Pd stoichiometry, which is believed to vary with the MFE, from 0.5 for large particles to 1 for very small ones showing predominence of edges and apices over faces. However, information may be obtained from the infrared spectrum of adsorbed CO; this molecular probe was used by Binet et al [10], with the help of spectral deconvolution, to evaluate the relative contributions of (111) faces, (100) faces and edges. Another study, performed in our laboratory [7] did not separate these contributions and focused on the pressure sensitivity of the linear and bridged species; it was shown that under carefully controlled pressure conditions, the CO/Pd ratio approaches unity on large particles, due to the presence of *compressed bridged* CO entities (every surface Pd being linked to *two* bridged species).The CO stoichiometry could then be taken as unity under definite conditions.

Third CO chemisorption by the carrier cannot generally be neglected when high reduction and/or outgassing temperatures are involved; this is particularly true on alumina as these pretreatments generate coordinatively unsaturated (cus) Al^{3+} ions acting as Lewis acceptor sites for CO [11, 12]. Previous experiments [12] showed, indeed, that γ- and η-aluminas prereduced by H_2 in the 573–773 K range are able to adsorb significant amounts of CO (up to 25 μmol per gram of alumina). This inconvenience can be removed by carrying out blank experiments and subtracting the amount measured on alumina from the quantity adsorbed on the catalyst. However, the presence of palladium may enhance the coordinative unsaturation of surface aluminium ions through pretreatments and the correction determined as above may then *underestimate* the amount of CO adsorbed on the carrier. Hence we have tried to assess this quantity from absorbance measurements as the spectrum of CO adsorbed on alumina consists of one band (A) in the 2 195–2 210 cm^{-1} interval (with a weak shoulder near 2 240 cm^{-1}) ascribed to CO-Al^{3+} species [7, 11, 12].

Figure 1 presents the variation of the integrated absorbance of (A) against the quantity of CO chemisorbed on γ-alumina prereduced at different temperatures; a linear relationship is observed. If the integrated absorbance of the same peak, measured on a Pd/γ-Al_2O_3 sample pretreated in the same conditions, is plotted versus the amount of CO chemisorbed on the carrier alone, the line obtained does not diverge significantly from the previous one. It follows that the presence of the metal has no noticeable effect on the quantity adsorbed by the carrier for reduction temperatures ⩽773 K. Therefore the MFE values presented in table I were obtained after correction of the CO amount adsorbed on the carrier alone.

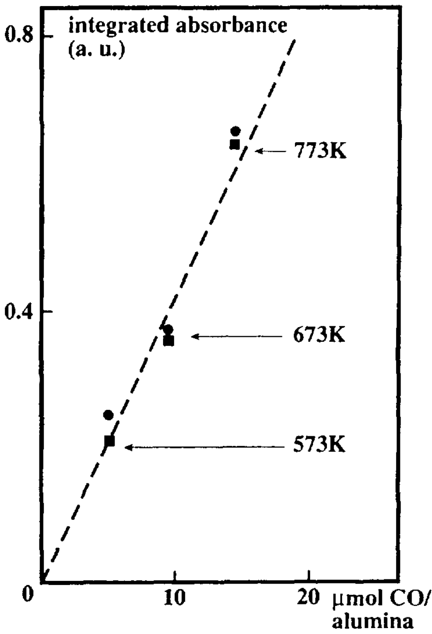

Fig 1. Variation of the integrated absorbance of CO adsorbed on alumina (2195–2110 cm^{-1}): (●) γ-alumina; (■) Pd/γ-alumina ex-Pd(acac)$_2$.

• *Correlation between the dispersion and the absorbance of the CO bands*

In a recent paper on supported platinum, Primet et al [13] reported a linear relationship between the optical density of the band ascribed to linear CO and the MFE of platinum. The bridged species could be neglected, due to their weak contribution to the overall absorption. In opposition with platinum, supported palladium generally presents an important contribution of bridged species [7, 10, 14, 15]. Working on palladium-alumina catalysts of low dispersion (<0.20), Palazov et al [15] reported empirical equations expressing a correlation between the number of CO molecules adsorbed on a definite crystal face in a particular mode and the integrated intensities of the respective bands. However, this interesting attempt could not apply to catalysts presenting a large interval of dispersion such as those prepared in the present work. Hence, we tried to draw a correlation between the *total* absorbance measured and the MFE, assuming CO/Pd equal to unity for the bridged species [7]. Results obtained on Pd–alumina catalysts reduced at various temperatures are shown in figures 2 and 3. The total absorbance is expressed as the integrated intensities of peaks assigned to linear (2100 cm^{-1}) and bridged species (2000–1700 cm^{-1}) adsorbed on palladium metal, without considering the small bands concerning ionic Pd [7]. All measurements were performed under 100 torr, taking into account the absorption of the gas phase and the bare sample. All data are given for the same palladium content, ie 15 μmol of Pd. It appears that the total integrated absorbance is proportional to the MFE deduced from the volume of adsorbed CO, after correction of the quantity adsorbed on the carrier. This relation holds for samples prepared from different precursors pretreated at the same temperature (fig 2) and for two samples pretreated at different temperatures (fig 3).

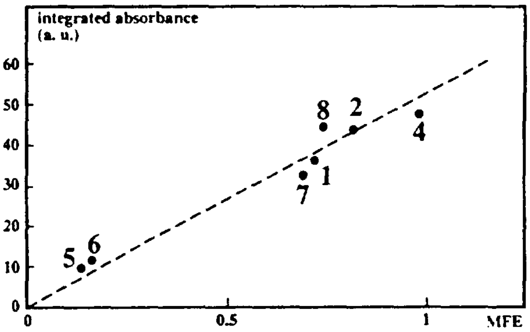

Fig 2. Variation of the integrated absorbance of the bands of CO adsorbed on palladium, in various Pd/alumina catalysts, against MFE. Reduction temperature: 573 K. The catalysts are numbered as in table I.

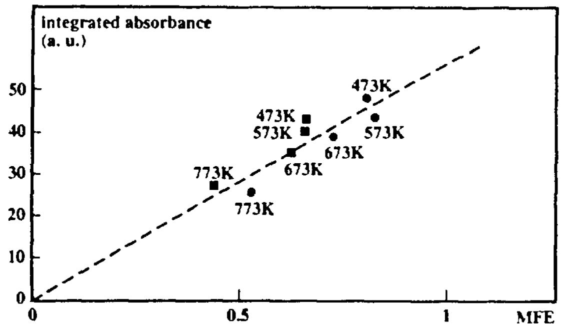

Fig 3. Variation of the integrated absorbance of the bands of CO adsorbed on palladium against MFE, for various reduction temperatures. (●) sample 2, (■) sample 7, as in table I (with results for Tr = 473 K instead of 373 K).

Working on various Pd–alumina samples, Duplan and Praliaud [16] obtained a linear relationship by plotting the *overall* integrated absorbance of bands of *irreversibly* adsorbed CO against the dispersion measured from hydrogen chemisorption; they reported a CO/H ratio of about 0.4 and a value as low as 0.2 for the linear/bridged (HF/LF) absorbance ratio. However previous results of our laboratory showed that outgassing at rt leads to a drastic decrease of the HF band (linear species), the LF peak being very little affected [7].

These findings explain the low values obtained by Duplan and Praliaud [16] (i) for the linear/bridged ratio (0.2) compared with ours (0.9) for the same reduction temperature and (ii) for the CO/H ratio. It is clear that the CO/H ratio depends strongly upon the procedure used through chemisorption measurements. Taking into account the amount of CO adsorbed on the carrier, we found it to be around 0.9 for samples 6 (MFE = 0.13) and 8 (MFE = 0.71). Hence the use of CO as a dispersion probe may be considered as reliable.

• *Precursor and reduction temperature effects on MFE*

Table I presents the MFE as expressed by the CO/Pd ratio (moles of CO adsorbed per mole of total palladium) for samples pretreated at various reduction temperatures.

It brings out the following points: (i) Pd nitrate is the only precursor leading to a low MFE; (ii) capillary impregnation by $PdCl_2$ gives rise to high MFE, which can be accounted for by an anion-exchange reaction occurring upon drying as shown by previous results [6, 17]; (iii) when the reduction temperature Tr increases from 373 to 573 K, the MFE increases for samples ex-$PdCl_2$, which should be ascribed to an incomplete reduction of Pd at Tr < 573 K [7]. In contrast, when $Pd(NO_3)_2$ is used as a precursor, the MFE decreases slightly when Tr increases. This finding is not surprising as these samples present larger PdO particles, in weak interaction with the carrier, which may be reduced easily even at room temperature [7]. The behavior of the sample ex-$Pd(acac)_2$ supported on η-alumina (sample 8) is, at first sight, unexpected as no residual anions are present after calcination. However, for this porous carrier, outgassing at 373 K does probably not allow cleaning up of the exposed metal atoms and the optimum outgassing temperature is about 573 K. It is also relevant to note that the sample 3 prepared by anion exchange maintains a high MFE up to 773 K and that in all cases the

Table I. Metal fraction exposed (MFE) for different catalysts and various reduction temperatures.

	Description of catalysts					*MFE after reduction at various temperatures (K)*			
Sample	*Precursor*	*Prep mode*	*Alumina*	*% Pd*	*% Cl*	*373*	*573*	*673*	*773*
1	$PdCl_2$	Capillary impregnation	γ	0.47	0.45*	0.67	0.70	0.60	0.38
2	$PdCl_2$	Capillary impregnation	η	0.67	1.88*	0.70	0.83	0.71	0.52
3	$PdCl_2$	Anion exchange	γ	0.24	0.33*	0.90	0.98	0.82	0.84
4	$PdCl_2$	Anion exchange	η	0.22	1.06*		1.00		
5	$Pd(NO_3)_2$	Capillary impregnation	γ	1.35	<0.02*	0.14	0.13	0.12	0.09
6	$Pd(NO_3)_2$	Capillary impregnation	η	1.30	<0.02*	0.18	0.16	0.13	0.13
7	$Pd(acac)_2$	Grafting	γ	0.45	<0.02*	0.66	0.65	0.63	0.44
8	$Pd(acac)_2$	Grafting	η	0.81	<0.02*	0.65	0.71	0.72	0.55
9	$PdCl_2$	Capillary impregnation	γ	7.07	1.25**			0.29	0.22

* Determined after reduction at 573 K; ** determined after reduction at 773 K.

porous carrier with the highest surface area gives the highest MFE (samples 2, 6 and 8).

According to Table II, the mean particle size obtained from TEM observations agrees reasonably well with the values deduced from CO chemisorption measurements using the relationship: d (nm) = 1.12/MFE [18] obtained by assuming a spherical shape and a mean number of Pd surface atoms equal to 14.5 per square nanometer [19].

Table II. Mean particle size of samples reduced at 573 K (carrier γ-alumina).

	Catalyst		*Mean particle size (nm)*	
Sample	*Precursor*	*% Pd*	*TEM*	*CO chem*
1	$PdCl_2$	0.47	1.8	1.6
7	$Pd(acac)_2$	0.45	1.5	1.7
5	$Pd(NO_3)_2$	1.35	10.6	8.6

However, in the case of palladium nitrate, the particle size distribution was not homogeneous, at variance with the findings of Lesage-Rosenberg et al [20] for a sample prepared in a similar way.

Hydrogenation of but-1-yne

The catalytic tests were performed at 278, 288 and 298 K. In all cases the products were but-1-ene, small quantities of butane and traces of *cis*-but-2-ene. At the end of the test, small quantities of liquid olefinic oligomers were detected at the reactor exit.

- *Induction or prestationary period*

When the samples were contacted with the reaction mixture, the activity was shown to increase for a long time, from 3 h to about 50 h. The duration of this prestationary period depends sharply upon the nature of the sample: short for the samples ex-nitrate and large (from 40–50 h) for the others. Figure 4 compares two typical samples (numbers 6 and 1). In addition a sample prepared by impregnation of silica (Aerosil 200) with $PdCl_2$ and pretreated in the same conditions shows a short induction period (about 3 h). In all cases, the selectivity measured during the prestationary period did not vary significantly from the values recorded at the stationary state.

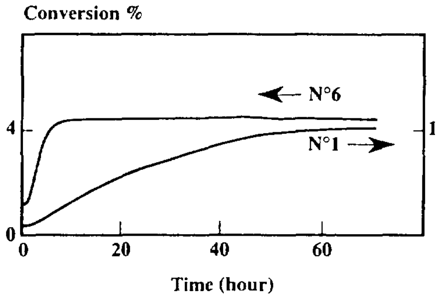

Fig 4. Variation of conversion at 278 K with time on stream for sample 1 and 6 showing differences in prestationary period (sample numbers refer to table III).

Several explanations may be put forward to account for this phenomenon:

(i) *The reduction of palladium*, not achieved by the pretreatment, could be completed during the prestationary period. The validity of this interpretation was tested by increasing the reduction temperature Tr in the case of the sample ex-acetylacetonate which suffers no significant dispersion losses when Tr increases; it was observed that increasing Tr from 573 K to 773 K does not change the prestationary period.

(ii) *Sintering* induced by the exothermicity of the reaction should lead to an activity increase. In fact, the TOF measured in the stationary state on a well-dispersed sample remained 20 times smaller than that of a sample of low dispersion (ex-Pd nitrate).

(iii) *Destruction of a strong metal-support interaction and/or reconstruction of the metal surface*: the duration of the prestationary period is small only when the metal–support interaction can be neglected, that is for alumina-supported palladium of low MFE (ex-Pd nitrate) and for the silica-supported sample. The prestationary period could then correspond to the breakdown of the metal–carrier interaction, ie, to the compensation of the electrodeficient character of the small metal particles through the adsorption of but-1-yne which acts as an electron donor. This activity increase must be related to the results obtained by Boitiaux et al [3] on Pd-alumina in the liquid phase. These authors, indeed, noticed that the TOF was higher when performing a second run. In addition, Hub et al [4], who worked on the same type of catalyst in the gas phase, carried out

Table III. Activity and selectivity of catalysts at 278 K.

Catalyst	*Precursor*	*% Pd*	*Reduction temperature (K)*	*MFE*	*TOF* (s^{-1})	*Selectivity in but-1-ene*	*Activation energy kJ.mol*$^{-1}$
1	$PdCl_2$	0.47	573	0.70	0.095	94.0	53
1b	$PdCl_2$	0.47	773	0.38	0.39	91.0	
2	$PdCl_2$	0.67	573	0.83	0.043	91.6	
3	$PdCl_2$	0.24	573	0.98	0.078	99.1	46
4	$PdCl_2$	0.22	573	1.00	0.048	98.6	
5	$Pd(NO_3)_2$	1.35	573	0.13	1.9*	98.3	46
6	$Pd(NO_3)_2$	1.30	573	0.16	1.7*	95.8	
7	$Pd(acac)_2$	0.45	573	0.65	0.27	98.4	53
8	$Pd(acac)_2$	0.81	573	0.72	0.082	97.4	42
9	$PdCl_2$	7.07	773	0.22	0.84	96.0	
9b	$PdCl_2$	7.07	673	0.29	0.77	96.0	

* Short prestationary period.

Table IV. Activity and selectivity of catalysts at 288 K: influence of the carrier and the reduction temperature.

Catalyst	*Precursor*	*Carrier*	*% Pd*	*Reduction temperature (K)*	*MFE*	*TOF* (s^{-1})	*Selectivity in but-1-ene*
5	$Pd(NO_3)_2$	γ-Alumina	1.35	573	0.13	3.5*	97.0
7	$Pd(acac)_2$	γ-Alumina	0.45	573	0.65	0.88	98.4
8	$Pd(acac)_2$	η-Alumina	0.81	573	0.72	0.23	97.4
8b	$Pd(acac)_2$	η-Alumina	0.81	773	0.55	0.25	98.3
11	$PdCl_2$	Silica	0.72	573	0.85	0.28*	98.4

* Short prestationary period.

a pretreatment involving a first catalytic run and an oxidation-reduction cycle to get reproducible results. Furthermore, in the course of a study on the hydrogenation of acetylene over Pd films, Janko et al [21] reported a reconstruction of the Pd surface (preferential development of the 111 plane) inducing a sharp increase of ethylene production. The 111 plane was thought to impede strong acetylene chemisorption. This explanation may account for our results but no experimental support is available.

- *Influence of the metal fraction exposed (MFE) on the turnover frequency (TOF) and the selectivity*

The conversion and the selectivity were measured after 50 h work, that is after the samples had reached the steady state. Figure 5 and table III show that the TOF decreases sharply when the MFE increases, in fair agreement with the findings of Boitiaux et al [3] in the liquid phase. A similar but less sharp trend was reported by Hub et al [4] with two Pd/alumina catalysts showing respectively 26 and 97% dispersion. It is also relevant to note that a marked drop of the TOF with the particle size was reported in the hydrogenation of vinylacetylene(but-1-en-3-yne) [22].

On the other hand, the activation energies (table III) measured at the stationary state in the 273–298 K range do not appear to depend upon the MFE. In addition, the selectivity in but-1-ene is unaffected by the MFE in the conversion range imposed by the differential conditions (⩽8%). This result is in accordance with the findings obtained with other types of reactors which showed no significant selectivity variation for conversion ⩽50% [3, 4].

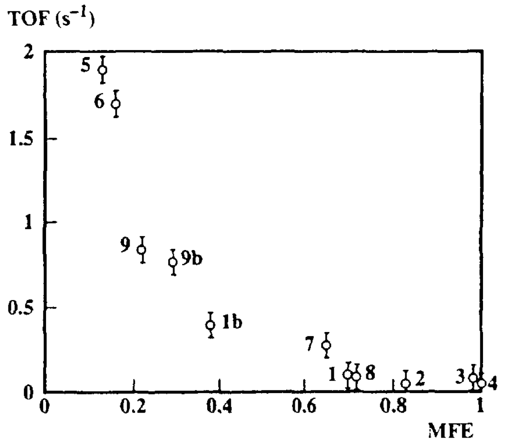

Fig 5. Variation of the TOF in the hydrogenation of but-1-yne against MFE for various catalysts numbered as in table III. Reduction temperature: 573 K, except for samples 1b, 9 and 9b. Reaction temperature: 278 K.

The drop in the TOF when increasing the MFE (fig 5, table III) may arise from different factors:

(i) *The lack of reduction* of palladium in samples showing high MFE values. This explanation can be considered when comparing samples 1 and 1b (ex-$PdCl_2$) in table III; previous results [7], indeed, have shown that residual ionic Pd is detected after reduction at 573 K (sample 1) and not after reduction at 773 K (sample 1b) while the TOF is four times larger for the latter. We compare now in table IV two ex-acetylacetonate catalysts: sample 8, which contains residual ionic Pd [7], and sample 8b which has not; in this case, the variations of TOF and MFE are weak. These results suggest that the presence of ionic Pd is not the only intervening factor. It may, however, reinforce the intrinsic electron-deficient character of small Pd particles (see below).

(ii) *The geometric effect*: if the adsorption of but-1-yne involves several palladium atoms, the TOF should decrease at high MFE. However, this effect should be observed only at very high MFE (>0.9) as particles of ca 10 Å contain about 40 metal atoms. In addition, a recent study by Hub et al [4b] suggested that the active site consists of only one Pd atom, in agreement with the conclusion of Guczi et al [23] in their study of the hydrogenation of acetylene on palladium.

(iii) *The role of palladium hydride*: it was first claimed that the formation of this species is unfavored on small Pd particles but an EXAFS study by Moraweck et al [24] on Pd/Y zeolite showed that a 0.4 H/Pd hydride was formed under 0.5 atm H_2 on very small particles (# 10 Å).

(iv) *Carrier effect*: small Pd particles gave low TOF for the three carriers used in the present work (γ-alumina, η-alumina, silica). As pointed out above, the nature of the carrier seems to influence only the duration of the prestationary period.

(v) *Precursor effect*: it has been shown that the nature of the precursor directly influences the MFE (Pd nitrate gives only low values) and the electronic state (some ionic Pd is left when starting from $PdCl_2$ and, to a lesser extent, from Pd acetylacetonate).

(vi) *Electron deficiency of Pd particles*: electron deficiency may arise either from the particle itself [25] (intrinsic deficiency) or from a metal-to-carrier electron transfer, which is significant only for very small particles. According to the data shown in table IV, the TOF measured at 288 K on Pd/silica- and Pd/η-alumina (samples 11 and 8) of comparable MFE do not differ significantly. Hence, the dominant factor responsible for the drop of TOF at high MFE seems to be the intrinsic electron-deficient character of small palladium particles. These findings are in agreement with the conclusions of previous investigations performed in the liquid phase [3] and the gas phase [4], and also with a study of the hydrogenation of vinylacetylene on Pd/alumina and Pd/silica [22].

Conclusion

The aim of this work was to deal with the intricate effects of the precursor, the carrier and the metal fraction exposed (MFE) in the selective hydrogenation of but-1-yne. It is confirmed that the turnover frequency (TOF) decreases markedly when the MFE increases. The nature of the precursor influences the TOF first through its effect on the MFE: palladium nitrate leads always to a low MFE, ie, to a high TOF; palladium chloride has a secondary effect as it leaves residual ionic palladium which tends to decrease the TOF. In addition to these effects, the nature of the carrier acts essentially upon the duration of the prestationary period: this period is particularly long in the case of alumina, when metal-to-carrier electron transfers are expected.

Finally, the decrease of TOF at high MFE is ascribed to the *intrinsic* electron deficiency of the metal particles even though the role of oligomer formation could not be discarded.

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