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On the deactivation of supported palladium hydrogenation catalysts by thiophene poisoning

X.L. Seoane [1]*, P.C. L'Argentiere [2], N.S. Fígoli [2] and A. Arcoya [1]

[1] *Instituto de Catálisis y Petroleoquímica, CSIC, Camino de Valdelatas s / n,*
Campus Universidad Autónoma Cantoblanco, 28049 Madrid, Spain
[2] *Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Santiago del Estero 2654,*
3000 Santa Fe, Argentina

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The deactivation of supported palladium catalysts for ethylbenzene hydrogenation by thiophene was studied. The presence of Pd^{n+} species on the catalyst surface, in samples prepared from acid solutions of $PdCl_2$, and reduced at temperatures below 450°C, was evidenced by XPS. A correlation between the concentration of electron-deficient Pd species and the sulfur resistance was found. Thus, the higher the value of the Pd^{n+}/Pd^0 ratio, the higher the sulfur resistance. Catalysts prepared from $Pd(NO_3)_2$ or from $PdCl_2$ reduced at 450°C, which essentially contain Pd^0, are more quickly deactivated. Furthermore, our results also suggest that while the influence of the metal dispersion on the stability of the palladium catalysts toward sulfur is not significant, the nature of the support, on the other hand, plays an important role.

Keywords: Pd catalysts; ethylbenzene hydrogenation; Pd deactivation; sulfur resistance; thiophene; XPS; electron-deficient Pd

1. Introduction

Several published papers show that catalysts containing electron-deficient metal atoms (Me^{n+}) on the surface, exhibit higher resistance to sulfur poisoning than those with metal atoms with a higher electron density [1–4]. Electron-deficient species may originate through the interaction of the reduced metal with electron-acceptor sites present on the support [5]. Recently, we have found that the rate of deactivation of several Pd/SiO_2 catalysts by thiophene, in the hydrogenation of ethylbenzene at 250°C, decreases when the concentration of Pd^{n+} sites increases [6].

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* To whom correspondence should be addressed.

The aim of the present work is to verify that the behaviour observed with silica-supported catalysts is also fulfilled with other supports of different chemical nature and textural and structural properties. To do this, we have prepared several palladium catalysts using α-Al_2O_3 and active carbon as supports. These catalysts, together with a Pd/γ-Al_2O_3 commercial sample, were reduced at different temperatures and their activity decay was evaluated during the hydrogenation of ethylbenzene in the presence of thiophene. Catalysts were characterized by gas chemisorption and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. CATALYST PREPARATION

Catalysts containing 0.3 wt% Pd were prepared by impregnation using the incipient wetness technique. An α-alumina support (T-708 Girdler Südschemie, SA = 10 m^2/g) was impregnated either with aqueous solutions of $PdCl_2$ (Catalysts Series CA) or $Pd(NO_3)_2 \cdot 6H_2O$ (Catalyst NA-2), in both cases at pH = 1. After drying at 120°C, the samples were calcined at 350°C in a dry air stream (500 ml/h g_{cat}) for 3 h. Samples CA were reduced at 250°, 350° and 450°C, in flowing hydrogen (50 ml/h g_{cat}) for 3 h. Sample NA-2 was reduced under the same conditions at 250°C. Two other catalysts containing 1.6 wt% Pd were prepared from $PdCl_2$ using carbon as support (CECA C-35, 1200 m^2/g BET surface area) and reduced (without the calcination step) at 250° and 450°C, respectively (samples CC). Experiments were also performed with two samples of a commercial catalyst, containing 0.3 wt% Pd on γ-Al_2O_3 which were reduced at 250° and 450°C (samples IS).

2.2. CATALYST CHARACTERIZATION

The degree of metal reduction was measured in a flow system with a thermal conductivity detector, heating 0.5 g of the precursor at 10°C/min in a 5% hydrogen in argon stream (60 cm^3/min), from 25°C up to its reduction temperature, which was then kept constant during 3 h. The degree of reduction was calculated from the total hydrogen consumption.

Metal dispersion was determined by the H_2–O_2 titration method [7], using the dynamic pulse technique [8]. The volume of hydrogen uptake was calculated from the integrated peak areas measured by means of a thermal conductivity detector. Samples of 0.5 g were reduced in situ under identical conditions to those used for the deactivation studies and then evacuated under an argon flow of 2 ℓ/h at 300°C, for 1 h. After cooling to 25°C, pulses of oxygen (300 μl) were introduced in the argon stream, until a monolayer of oxygen was formed. After heating to 100°C, titration of oxygen was performed by injection of pulses of 300 μl of a mixture of Ar + 5 vol% H_2 into the carrier argon stream. Under these conditions, the β-palladium hydride phase is not substantially formed and, if formed, it is rapidly eluted from the surface [7,9]. Furthermore, for the supports used no adsorption of hydrogen was observed. Prior to its use each gas was carefully purified. The reaction taking place is

$$PdO + \tfrac{3}{2}H_2 \rightarrow PdH + H_2O. \tag{1}$$

Thus, the dispersion was calculated assuming a stoichiometry $H_2/Pd = 3/2$.

XPS spectra were obtained using a Shimadzu ESCA 750 electron spectrometer and processed with a Shimadzu ESCAPAC 760 data system. The C 1s line at 285.0 eV was taken as an internal standard and was used to correct the possible deviations caused by electric charge of the samples. The position of the peak maxima and the full width at half-maximum intensity (FWHM) of the Pd $3d_{5/2}$ peak were used to follow the superficial electronic state of Pd. After reduction, the samples were introduced into the sample holder under isooctane and protected from exposure to air by a meniscus of this liquid. Isooctane was removed during pumping in the preparation chamber of the XPS equipment. This operating procedure ensures [10] that there is no modification of the electronic state of palladium which is fairly stable. Anyhow, exposing the catalysts after reduction to the atmosphere for different periods of time confirmed that there were no electronic modifications of palladium, as observed by other authors for several palladium supported catalysts [11–13].

2.3. CATALYST DEACTIVATION

The stability of catalysts was evaluated in the hydrogenation of ethylbenzene (ETB) containing 100 ppm of thiophene. Experiments were carried out in a fixed-bed tubular reactor containing 10 g of catalyst (particle size 1.41–2.0 mm) diluted with SiC. The reaction conditions were 3 MPa; molar ratio $H_2/ETB = 10$; temperature 250°C and liquid space velocity 3 h^{-1}. ETB was diluted with decalin (70 wt%). To follow the change of catalytic activity with the time on stream, product samples were periodically collected and analysed by gas chromatography. Practically, the only product of the reaction in all the experiments was ethylcyclohexane.

We did carry out several preliminary experiments to look for any external and internal diffusion control, following the conventional methodology [14]: (a) At constant F/W (h^{-1}) and H_2 to liquid hydrocarbon ratio, but changing both the liquid flow and catalyst weight, between 30/10 and 90/30. The conversion remained constant. (b) Using different catalyst particle sizes between 3.5 and 1.0 mm. The conversion increased in going from 3.5–2.38 mm to 2.38–2.0 mm and then remained constant. (c) With the contaminated feed, using the standard experimental conditions and two different particle sizes: 2.0–1.41 and 1.41–1.0 mm. The curves of conversion decay versus time obtained for both particle sizes

Table 1
Catalyst characterization and deactivation kinetics results

Catalyst	Support	T_r (°C)	D (%)	Pd $3d_{5/2}$ (eV)	FWHM (eV)	k'_d (h^{-1})
CA-2	α-Al_2O_3	250	9.2	337.9	3.9	1.50
CA-3	α-Al_2O_3	350	8.4	337.4	3.5	1.70
CA-4	α-Al_2O_3	450	7.7	335.9	2.2	2.06
NA-2	α-Al_2O_3	250	21.7	335.1	2.0	2.15
CC-2	carbon	250	17.7	338.3	3.7	0.82
CC-4	carbon	450	14.2	335.4	2.0	2.20
IS-2	γ-Al_2O_3	250	44.0	336.2	2.8	0.98
IS-4	γ-Al_2O_3	450	42.1	335.4	2.0	2.02

were practically coincident. (d) The γ-Al_2O_3 and carbon deactivated catalysts (IS-2 and CS-2) were charged again in the reactor and the reaction was carried out in the standard conditions. In both cases, the conversion was zero. Thus, the results obtained showed that, in our experimental conditions, both external and internal diffusional limitations were absent, and a homogeneous distribution of the liquid in the reactor was attained.

3. Results

3.1. CHARACTERIZATION

The measurements of the degree of reduction of the samples showed that the reduction of palladium was complete in all cases (> 95%). Table 1 summarizes the metal dispersion (D (%)) and the binding energy (BE) and the full width at half maximum intensity (FWHM) values for Pd $3d_{5/2}$. Except for the γ-alumina catalysts, all catalysts had a low degree of dispersion, which was, however, higher when nitrate was used as precursor. It can also be seen that the reduction temperature, up to 450°C, has only a slight effect on the metal dispersion.

Catalysts reduced at 250°C, except for NA-2, display BE values higher than 336.0 eV, suggesting that these catalysts have different amounts of Pd^{n+} species on the surface. The BE = 335.1 eV value in NA-2 indicates that all the palladium is found as Pd^0. The shift of the BE towards higher values when the temperature of reduction decreases indicates that the ratio Pd^{n+}/Pd^0 in the catalysts increases accordingly.

The presence of electron-deficient metal species on the surface of reduced catalysts prepared from acid solutions of $PdCl_2$ has been reported in the literature [15]. Experimentally, we have verified the stoichiometric reduction of unsupported $PdCl_2$ at room temperature. In supported catalysts, however, some stable species Pd^{n+} remain on the surface, even in carefully reduced samples [16].

3.2. CATALYST DEACTIVATION

Figs. 1a and 1b show the change of conversion of ETB to ethylcyclohexane in the presence of 100 ppm of thiophene versus time on stream, for Pd/α-Al_2O_3, Pd/γ-Al_2O_3 and Pd/C. A progressive loss of activity due to the toxic effect of thiophene is found in all cases. Preliminary experiments performed in the absence of thiophene allowed us to verify that catalyst deactivation is essentially produced by sulfur and not by coke deposition. The loss of activity is not due to Pd agglomeration. Thus, the sulfur deactivated IS-2 catalyst, calcined and reduced like the fresh catalyst, gives the original dispersion and the same initial activity.

The kinetic analysis of the catalyst deactivation is based on the model proposed by Levenspiel for the side-by-side poisoning, which assumes separable kinetics and a potential law [17]. Catalyst deactivation takes place simultaneously to the main reaction

$$\mathrm{ETB} + \mathrm{H_2} \xrightarrow{k} \mathrm{ETCH}, \tag{2}$$

$$\mathrm{Th} + \mathrm{Cat} \xrightarrow{k_d} \mathrm{Th \cdot Cat}. \tag{3}$$

Under these conditions, the overall rate of hydrogenation of ethylbenzene $(-r)$, at constant temperature, is a function of both the time on stream (t) and the position in the catalyst bed, this latter characterized by the space time. The separability means that the catalyst surface is ideal in terms of Langmuir type of adsorption [18]. Thus, in the presence of a poison, the catalytic activity of a given metal site for the hydrogenation reaction is not modified by the poisoned neighbouring sites. In this case, the main reaction rate at the time t, $(-r)$, is

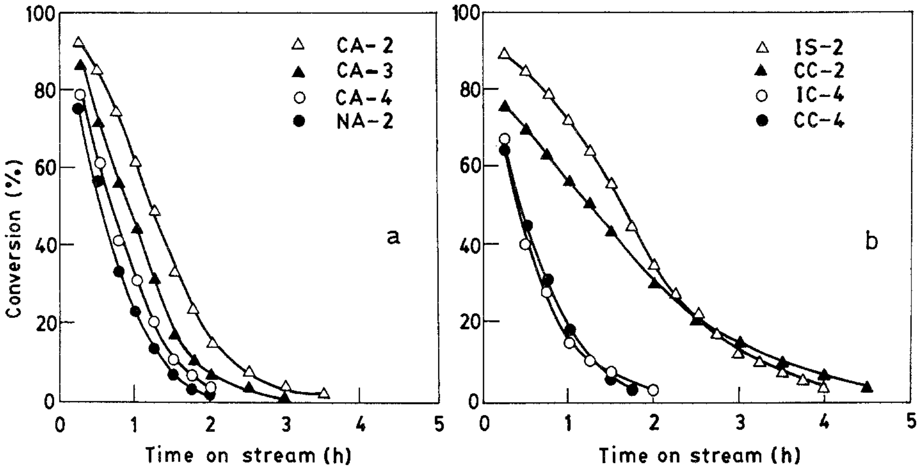

Fig. 1. Deactivation curves of catalysts. (a) α-Al_2O_3 support; (b) carbon (CC) and γ-Al_2O_3 (IS) supports.

simply the rate at time $t = 0$ multiplied by an "activity factor" (a), that measures the fraction of the initial active sites still available at the time t.

The rate of the hydrogenation reaction on the fresh catalyst in the absence of sulfur $(-r_0)$ is

$$(-r) = (-r_0) = -\mathrm{d}C_{\mathrm{ETB}}/\mathrm{d}(W/F) = kC^{n}_{\mathrm{ETB}}, \tag{4}$$

since hydrogen is in a large excess. As the activity of the catalyst is defined as

$$a \equiv (-r)/(-r_0) \tag{5}$$

(at $t = 0$, $a = 1$ and $(-r) = (-r_0)$) the overall rate of disappearance of ethylbenzene at time t, can be written as

$$(-r) = (-r_0)a = kC^{n}_{\mathrm{ETB}}a. \tag{6}$$

The rate at which the active sites are poisoned is given by

$$-r_{\mathrm{d}} = -\mathrm{d}a/\mathrm{d}t = k_{\mathrm{d}}C^{m}_{\mathrm{Th}}a^{\mathrm{p}} = k'_{\mathrm{d}}a^{\mathrm{p}}. \tag{7}$$

The thiophene concentration (C_{Th}) along the reactor can be taken as constant due to the small size of the catalyst particles, the high feed flow rate and the fact that the deactivation rate is small compared with the reaction rate (the time on stream is greater than the space time). On the other hand, this kinetic analysis is used to compare the rate of deactivation of a family of catalysts under the same reaction conditions. Thus, we can reasonably assume the above approximation [19–22].

For $p = 1$, we have from eq. (7)

$$a = \exp(-k'_{\mathrm{d}}t). \tag{8}$$

Assuming that there is no appreciable change of volume in the reactor, $C = C_0(1 - x)$, and taking $n = 1$, after substituting (8) in (6), we obtain for the tubular reactor

$$(-r) = C_0\,\mathrm{d}x/\mathrm{d}(W/F) = kC_0(1 - x)\exp(-k'_{\mathrm{d}}t), \tag{9}$$

where C_0 (g/g) is the concentration of ethylbenzene in the liquid feed; x, ETB fractional conversion; W (g), weight of catalyst; F (g/h), total liquid flow rate; k (h^{-1}), hydrogenation rate constant; k'_{d} (h^{-1}), deactivation rate constant; t (h), time on stream. Upon integration of eq. (9):

$$\ln\ln[1/(1 - x)] = \ln(kW/F) - k'_{\mathrm{d}}t. \tag{10}$$

A plot of $\ln\ln[1/(1 - x)]$ versus time for each catalyst yields a straight line (figs. 2a–2c) which confirms the validity of eq. (9). From the slopes of the straight lines, the values of k'_{d} given in table 1 were calculated.

We have verified that other kinetic equations derived for other values of p and n do not account equally well for all our experimental data, or do not fit them at all. Zero or first order reactions with respect to aromatics are frequently given in the literature [23,24]. On the other hand, according to Khang and

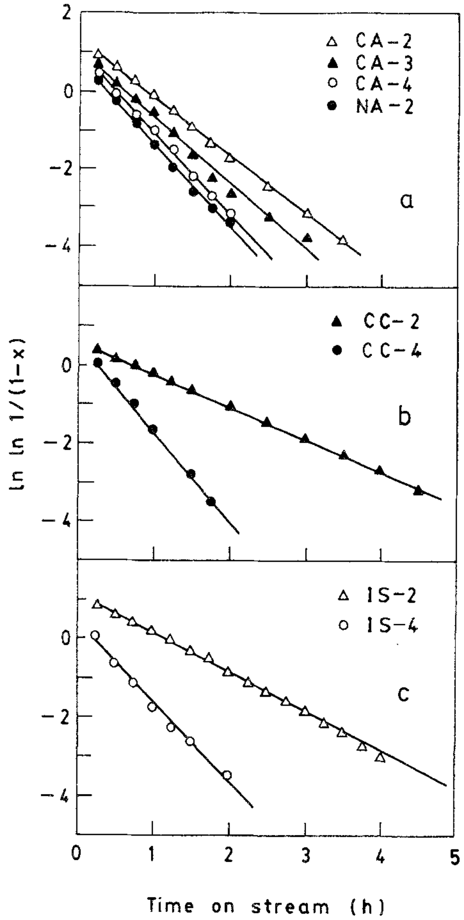

Fig. 2. Fitting of kinetic equation (9).

Levenspiel [25] an order of deactivation $p = 1$ for side-by-side deactivation indicates that the poisoning process is not diffusion limited.

The Levenspiel model is a simple and very useful method to compare the deactivation of a set of catalysts of the same type, specially of monofunctional catalysts such as those used in this work [26,27]. Another valuable approach derived from the plot of normalized activity versus molecules of thiophene fed per initial exposed metal atom, is also frequently used [4,28,29]. According to ref. [28], however, a kinetic model for deactivation provides a more quantitative method for comparing the sulfur resistance of different catalysts and estimating their pocess life in the presence of sulfur poisons. It allows us to determine the deactivation rate constant (k_d'), which is an intrinsic measure of resistance to sulfur poisoning [28]. In fact, sulfur resistance is related to the reciprocal value of k_d', that is, the lower the value the more sulfur resistance, and its meaning could be associated to a sort of mean lifetime or the average life expectancy of an exposed metal atom of the fresh catalyst.

Thus, if we assume that the stability of a metal towards sulfur can be related to the kinetics of the reaction [30]

$$n\mathrm{Me}^0 + \text{“S”} \rightleftharpoons \text{“Me}_n\text{S”}, \tag{11}$$

then, whatever the formula “Me$_n$S” means, either a chemical compound or a surface adlayer, the lower the k_d' value the slower the formation of the inactive species “Me$_n$S” and the higher the sulfur resistance.

4. Discussion

The generally accepted mechanism for metal poisoning by sulfur at temperatures about $T > 150°\mathrm{C}$ involves a strong chemisorption of the poison molecule on the metal, eventually followed by its hydrogenolysis [30], leading to an inactive metal sulfur species (eq. (11)). On this basis, an interpretation of our results can be suggested: the lower the electron density of the surface palladium atoms the weaker the metal–sulfur bond and hence the higher the sulfur resistance. Thus, the catalysts reduced at lower temperatures have a higher concentration of electron-deficient palladium atoms (Pd^{n+}) and they are the most refractory to poisoning.

For each family of catalysts, sulfur resistance correlates with the chemical state of surface Pd rather than with metal dispersion, as shown in fig. 3 where the values of k_d' versus dispersion are depicted. For example, catalysts CA-2,

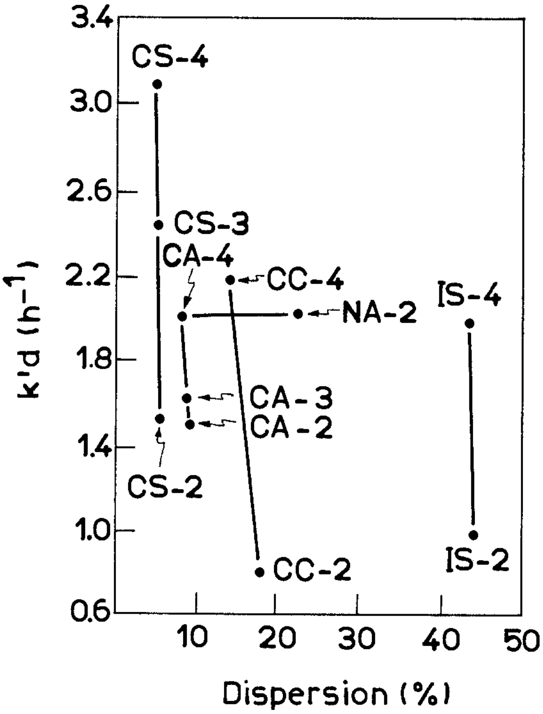

Fig. 3. Effect of the palladium dispersion on the deactivation rate constants.

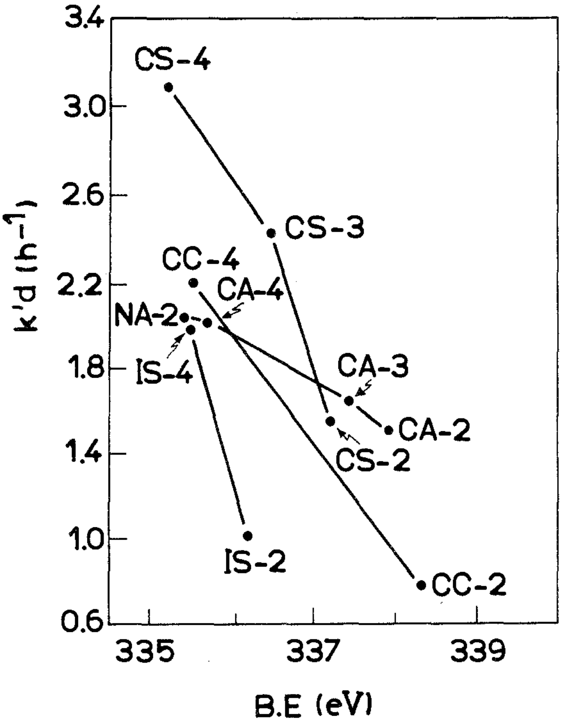

Fig. 4. Effect of the surface chemical state of palladium on the deactivation rate constants.

CA-3 and CA-4 have different values of k'_d in spite of the fact that they have similar dispersion. But these samples have, nevertheless, different values of the BE, from which one can deduce that the value of the ratios Pd^{n+}/Pd^0 on the surface must also be different.

These findings are also observed in fig. 4, in which values of k'_d versus the BE of Pd $3d_{5/2}$ for the different supports are plotted. For comparative purposes, the previously obtained values for Pd/SiO_2 [6] are also shown (series CS). For each support, the higher the value of Pd^{n+}/Pd^0, the higher the sulfur resistance. The presence of electron-deficient Pd atoms strongly inhibits the interaction palladium–thiophene, either by an electronic effect, decreasing its electron-donor character, or by a geometrical effect, diminishing the size of the ensembles of Pd^0 required for the hydrogenolysis of thiophene [31]. The result is a catalyst less sensitive to the poison. On the other hand, catalysts NA-2, CC-4 and IS-4 show a poor stability, despite their relatively high activity and dispersion. This may be due to the fact that their active surface is essentially formed by metallic palladium (Pd^0).

The presence of electron-deficient species on the catalyst surface is well documented in the literature [32]. Frequently, the mechanism of formation is associated with the existence on the surface of some type of acid or electron-acceptor sites (s), that interact with the metal through an electrostatic polarization or charge transfer [1–3,5]:

$$Me^0 + s \leftrightarrow Me^{n+} \ldots s^{n-}. \tag{12}$$

In Pd catalysts prepared by impregnation from acid solutions of $PdCl_2$, the presence of oxidized forms of Pd was also reported [15,33]. We have found Pd^{n+} species (and Cl^-) in catalysts prepared by this technique and reduced at temperatures below 450°C, but not in those prepared from $Pd(NO_3)_2$ [16]. Several hypotheses could be mentioned to explain the presence of oxidized Pd species on the surface, in spite of the easy reduction of the $PdCl_2$ [34–36]. For example, the interaction of Pd with support-fixed protons coming from the impregnating acid solution. This interaction can take place through bridge-like structures, since the difficulty to eliminate thermally the hydrogen chloride adsorbed on the catalyst is well established,

$$Pd^0 + H^+ + Cl^- \longrightarrow Pd^{n+} \ldots H^{(1-n)+} \ldots Cl^-. \tag{13}$$

Actually, this mechanism is similar to the one recently suggested by Homeyer et al. [37], in which part of the protons formed during the reduction of Pd^{2+} remain adsorbed in the vicinity of the palladium atoms and form an adduct with the metal particles. The positive charge is distributed over the adduct, which will thus be electron-deficient.

In any case, whatever the exact mechanism is, the positive effect of chloride ions has been confirmed. It seems likely that the role of the chlorine anions could be to stabilize the positively charged palladium structures, resulting in more thioresistant catalysts [33,36]. Therefore, for each one of the supports used in this work, our results show that there is a positive correlation between temperature of reduction, concentration of oxidized palladium and sulfur resistance, such as was found for silica.

Now, even though our results highlight the close relationship existing between the surface chemical state of palladium and the thioresistance, actually that property is not the only that determines the stability of the catalyst towards sulfur poisoning. In fact, our work also brings about the importance of the carrier for the stability of catalysts. Thus, samples with similar values of BE (CC-2 and CA-2) but with different supports have different values of k'_d.

The influence of the support on the physicochemical properties and, therefore, on the catalytic behaviour of metals is now recognized [5,38]. Specific support properties such as chemical nature, texture, pore structure, surface state, etc., can indeed modify the dispersion, morphology and/or localization of the metal particles, electronic structure of the surface palladium atoms, adsorption–desorption equilibria of reactants and/or poison, etc., in a different way, whereby different values of thioresistance can arise. Thus, as our results reveal, the resistance of palladium supported catalysts to thiophene poisoning is a complex property of the whole catalyst, which cannot be related to a single parameter. Accordingly, an ultimate explanation of the palladium poisoning by sulfur is still far from being completely satisfactory.

5. Conclusion

The results obtained in this work with Pd/α-Al_2O_3, Pd/C and Pd/γ-Al_2O_3 catalysts strengthen the behaviour previously observed with Pd/SiO_2. Namely, for each support a correlation between reduction temperature, concentration of surface electron-deficient palladium (Pd^{n+}) and resistance towards thiophene does exist. In catalysts prepared from $PdCl_2$ the chlorine species likely stabilize the oxidized forms of Pd. These Pd^{n+} species are not observed when $Pd(NO_3)_2$ is used as precursor. The surface chemical state of Pd, however, is not the only catalyst property that determines its stability. Actually, as our results show, the support also plays an important role with regard to the sulfur resistance of palladium catalysts used in ethylbenzene hydrogenation.

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