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Influence of the Reaction Conditions and Catalytic Properties on the Liquid-Phase Hydrodechlorination of Chlorobenzene over Palladium-Supported Catalysts: Activity and Deactivation

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The liquid-phase hydrodechlorination of chlorobenzene with molecular hydrogen was studied over palladium-supported catalysts. The reaction takes place at a gradually decreasing rate through progressive poisoning of the active phase by chloride ions. It is found that the correct choice of the metallic precursor (free of chloride ions) is crucial for the optimum performance of the final solid obtained. In addition, a better resistance to chlorine is observed when the size of the metallic particle increases. The supports tested, viz. $SiO_2/AlPO_4$, ZrO_2, and MgO, significantly affected catalyst deactivation. Thus, supports that can capture chloride species (e.g., ZrO_2) allow the reaction to finalise within relatively short times. The reaction appeared to be structure-sensitive in regard to the initial activity. Changing dispersion from 54 to 7% was accompanied by an increase in catalytic activity by a factor of 20.

Key Words: **hydrodechlorination; chlorobenzene; palladium catalyst; structure sensitivity; deactivation.**

INTRODUCTION

Hydrodehalogenation, also called hydrogenolysis, is the most promising method for detoxifying organohalogen waste (1). Together with ecological safety, it often ensures complete regeneration of the initial raw material, which may open new avenues for the development of low-waste technologies. Occasionally, hydrogenolysis yields products of industrial interest.

Hydrogenolysis can be effected by thermal, catalytic, and reactive procedures. The last involve the use of expensive hydrogen donors such as $LiAlH_4$ or $NaBH_4$ and are only of preparative significance. In this work, we focused attention on the catalytic hydrogenolysis of organohalogen compounds, which are of the utmost practical importance. There are a large number of reported catalytic hydrogenolysis processes that are implemented in either the gas (2) or liquid phase (3) and use a wide variety of catalysts. The hydrogen source can be molecular hydrogen (4) or indeed any other hydrogen donor such as a formate salt (5), a hypophosphite salt (6), etc.

There is no general consensus about the structure sensitivity of the hydrodechlorination reaction (7–14). Thus, some authors present data that indicate that the reaction is structure-sensitive (7–11) while others have suggested that the reaction is structure-insensitive (12–14). The results reported in the literature are difficult to compare. The reaction conditions, including gas- or liquid-phase reaction, catalyst support, reactants for which the hydrodechlorination is studied, etc. vary from one study to another, making it difficult to obtain a unified picture of the chemistry involved. The central roles of the catalyst preparation procedure and modification warrant in-depth investigation with a view to acquiring a better understanding of the actual affect of particle size on catalytic activity.

The inhibitory effect of hydrogen halides on hydrogenolytic processes has traditionally been ascribed to their adsorption on the catalyst surface and consequent blocking of its active sites (1). Blocking of these sites by the hydrogen halide can be avoided by, for example, using an additive such as NaOH (4). Little research, however, has so far been conducted into the relationship between catalyst deactivation and metal particle size or on the influence of the support on the blocking of active sites. Deactivation phenomena, the regeneration of deactivated catalysts, and the development of poison-resistant catalytic systems are all of a high practical significance.

This paper reports on the liquid-phase hydrogenolysis of chlorobenzene over six different palladium-supported metal catalysts. The catalytic systems studied were intended to provide valuable information about the structure sensitivity of the reaction in relation to catalyst preparation variables such as the metal precursor, metal loading, type of support, and presence of additives. Special attention was also given to deactivation phenomena, which were studied

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TABLE 1

Textural and Surface Chemical Properties of the Supports: Specific Surface Area (S_{BET}), Cumulative Pore Volume (V_p), Mean Pore Radius (r_p), and Surface Acidity and Basicity as Measured by TPD Using Pyridine (PY) and CO_2, Respectively

	Textural properties			Acid–base properties	
Support	S_{BET} ($m^2\ g^{-1}$)	V_p ($ml\ g^{-1}$)	r_p (A)	Acidity (μmol of PY g^{-1})	Basicity (μmol of CO_2 g^{-1})
PM2	413	0.69	60	115	—
PM2(Na)	272	0.53	52		
MgO	111	0.37	83	35	506
ZrO_2	127	0.10	28	49	91

in terms of metal particle size and the acid–base properties of the catalyst support.

EXPERIMENTAL

Synthesis and Characterization of Catalysts

The supports for the metal catalysts were three solids of different acid–base properties, namely, zirconium oxide calcined at 673 K *in vacuo*, magnesium oxide calcined at 873 K in an air stream, and a mixed system consisting of aluminium orthophosphate and silica in a 20 : 80 ratio by weight that was named PM2. The procedure used to prepare the supports was described in detail in previous papers (15, 16). A portion of the PM2 system was modified by impregnation with a methanol solution of NaOH containing the amount of alkali required to ensure a sodium content of 5% by weight in the final solid. The modified system was named PM2(Na).

The supports were used to prepare metal catalysts by depositing palladium by the incipient wetness impregnation method. The metal precursor was either palladium chloride (label (A) in the catalyst name) or palladium acetylacetonate (label (B) in the catalyst name). The support was placed in a flask and supplied with an appropriate amount of metal precursor dissolved in acetone. The flask was then placed in a rotavapor equipped with a water bath at 318 K and spun for 6 h. Next, the solvent was evaporated *in vacuo* and the residue dried in a stove at 383–393 K for 24 h, ground, and sifted to a fine powder. Finally, the powder was calcined in an air stream (flow rate 50 ml min^{-1}) by raising the temperature linearly to 573 K and then holding it for 2 h. The catalysts thus obtained were reduced in a hydrogen stream at 120 ml min^{-1}. The reduction program started at 373 K, which was held for 1 h and then raised to 493 K linearly at 2 K min^{-1}, the final temperature being held for 10 min. Finally, the reduced solids were cooled in a hydrogen stream. Temperature-programmed reduction (TPR) experiments confirmed that the temperature used resulted in the thorough reduction of supported palladium in all the systems studied.

The textural properties of the supports and metal catalysts were determined from nitrogen adsorption–desorption isotherms run at the liquid nitrogen temperature on a Micromeritics ASAP 2000 instrument. Their specific surface areas (S_{BET}) were obtained by the BET method (17).

The acid–base properties of the supports were determined by temperature-programmed desorption of probe molecules in conjunction with mass spectrometry (TPD–MS) as described elsewhere (18, 19). The probes used were pyridine for acid sites and carbon dioxide for basic sites. The results are summarized in Table 1.

The metal properties of the catalysts, viz. mean particle size (d), metal surface area (S_{MET}), and metal dispersion (D), were determined by hydrogen chemisorption (pulse method) at 373 K on a Micromeritics TPD/TPR 2900 analyser (see Table 2). The mean metal particle diameter (d_{MET}) was calculated, assuming spherical geometry, from the equation $d_{MET} = 6/(S_{MET}\rho)$, where ρ is the palladium specific mass (11.97 g/cc). Dispersion was calculated according to the equation $D(\%) = 112/d_{MET}(\mathrm{nm})$.

Procedure

Liquid-phase hydrogenations of chlorobenzene with molecular hydrogen were carried out in a model 3911 low-pressure reactor from Parr Instruments Co. at a constant rate of 300 shakes min^{-1}. The reaction vessel (500-ml volume) was wrapped in a metal jacket through which

TABLE 2

Specific Surface Area (S_{BET}), Mean Metal Particle Diameter (d_{MET}), Metal Surface Area (S_{MET}), and Metal Dispersion (D) of the Palladium-Supported Catalysts Studied

Catalyst	S_{BET} ($m^2\ g^{-1}$)	d_{MET} (A)	S_{MET} ($m^2\ g_{Pd}^{-1}$)	D (%)
$Pd_{0.5}$/PM2(B)	423	34	146	33
Pd_1/PM2(B)	419	36	136	31
Pd_3/PM2(B)	387	43	114	26
Pd_3/PM2(A)	325	25	201	45
Pd_3/PM2(Na)(B)	264	21	243	54
Pd_3/PM2(Na)(A)	192	102	50	11
Pd_3/MgO(B)	84	34	154	33
Pd_3/ZrO_2(B)	119	31	161	36

thermostated water was circulated. The apparatus was equipped with a gauge that recorded the pressure inside the reaction vessel throughout the experiments.

All reactions were conducted with an overall liquid volume of 20 ml, a 0.5 M chlorobenzene concentration in methanol, an initial hydrogen pressure of 0.414 MPa, and a temperature of 313 K.

Prior to each reaction, an amount of 100 mg of previously reduced metal catalyst was activated in a hydrogen stream at 120 ml $\min^{-1}$ at 393 K for 15 min and then cooled in the same gas stream.

The standard operational procedure used in each experiment was as follows: the reaction vessel was loaded with 20 ml of 0.5 M chlorobenzene and 100 mg of catalyst (previously activated in the hydrogen stream). After the temperature levelled off at 313 K, which took about 10 min, the reaction vessel was evacuated and filled with hydrogen to a pressure of 0.414 MPa. Five minutes later, the shaking device was started and the reaction timed. In each reaction, the amount of chlorobenzene that was converted over the contact period prior to shaking ($10 + 5$ min) was measured.

Blank tests intended to ascertain that the reaction did not take place thermally in the absence of catalysts were conducted when the reaction mixture consisted solely of the substrate and solvent. No signs of reaction were detected after 6 h under these conditions.

The absence of intraparticular and interparticular diffusion under the operating conditions used was also checked. The particle size of the catalysts was always small enough (less than 0.149 mm) to ensure negligible intraparticular diffusion (4). On one hand, the specific rate, r_g (mmol s^{-1} g_{Pd}^{-1}), was found not to depend on the shaking rate above 200 shakes/min. On the other hand, the overall rate was also found to be dependent on the amount of catalyst used (50–150 mg), the two being related by a straight line with a correlation coefficient greater than 0.99. This linear relationship suggests that the dehalogenation rate was kinetically controlled over the catalyst weight range tested (3).

Analysis of Reaction Products

Reaction products were analysed on a Fisons Instruments CG 8000 series gas chromatograph furnished with a 30-m long × 0.53-mm i.d. A Supelcowax-10 semicapillary column was fitted to an FID detector. Products were quantified with cyclohexane as an internal standard.

RESULTS AND DISCUSSION

Characterization of Catalysts

The textural and physico–chemical properties of the supports as well as the metal properties of the catalysts are summarized in Tables 1 and 2. Note that the supports differed markedly in their acid–base properties. Thus, PM2 contained acid sites only, whereas the magnesium oxide contained mostly basic sites and the zirconium oxide was amphoteric, with both acid and basic sites.

Regarding specific surface areas, the aggressiveness of NaOH doping on PM2 significantly decreased its S_{BET} (from 413 to 272 m^2 g^{-1}). Unlike the acetylacetonate, impregnation of the support with palladium chloride as the metal precursor caused an additional decrease in the specific surface area.

Hydrogenolysis of Chlorobenzene

The reaction order with respect to the hydrogen pressure was obtained from the slope of the logarithmic plot of the initial reduction rate (r_g) against the hydrogen partial pressure (0.276–0.551 MPa), using a 0.5 M chlorobenzene concentration in methanol and 100 mg of catalyst Pd_3/PM2(B) at a constant temperature of 313 K, conditions under which the resulting reaction order was 1 ($r = 0.95$). Similarly, the reaction order in chlorobenzene was determined by using substrate concentrations over the range 0.3–0.9 M. The reaction order thus found was zero ($r = 0.91$); i.e., r_g was independent of the substrate concentration over the range tested, which suggests that chlorobenzene was strongly adsorbed on the catalyst surface.

The kinetic study was completed by calculating activation parameters such as the apparent energy ($E_a = 25.9 \pm 4.7$ kJ mol^{-1}), apparent enthalpy ($\Delta H^{\#} = 23.3 \pm 4.7$ kJ mol^{-1}), and apparent entropy of activation ($\Delta S^{\#} = -185.7 \pm 15.2$ J mol^{-1} K^{-1}) from the Arrhenius and Eyring equations for the catalyst Pd_3/PM2(B).

The study of the hydrogenolysis of chlorobenzene was started by recording the distribution profile for the products (benzene and chlorobenzene) at a variable reaction time (Fig. 1). The hydrogenolysis developed at rates up to 40% conversion, above which the process slowed down. The profile was used as a basis to determine the influence of synthetic and catalyst composition variables such as the palladium content, metal precursor, support, and its doping on the reaction rate and hence on the catalyst activity (expressed as turnover frequency).

Table 3 reflects the effect of the palladium content, metal precursor used in the impregnation procedure, and doping of the support with 5% Na on the catalytic activity. All data correspond to support PM2.

Influence of the Palladium Content

Figure 2 shows the variation of the proportion of benzene (as molar %) with the reaction time obtained for three similar catalysts containing 0.5, 1, and 3% of Pd nominal. As can be seen from Table 2, the metal dispersions obtained with the three catalysts were comparable (33, 31, and 26%, respectively). The molar conversion obtained after such a long reaction time as 990 min, X_{990}, differed markedly among the three catalysts, ranging from 1% for

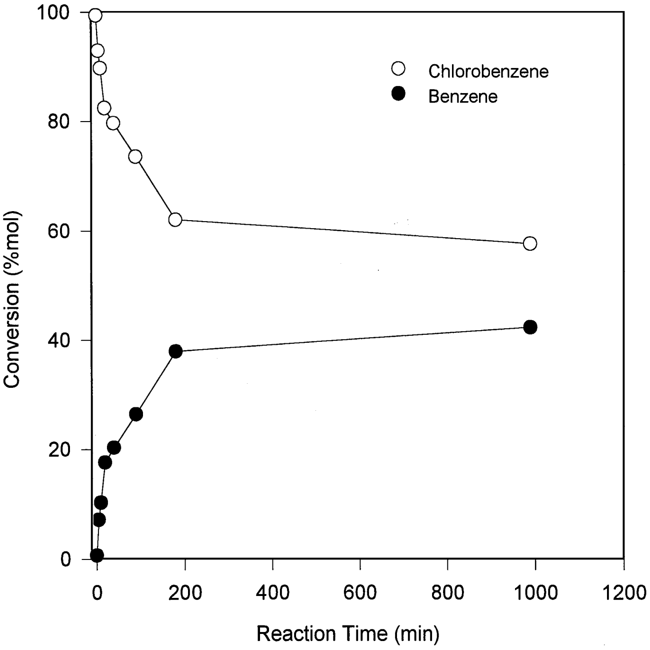

FIG. 1. Temporal variation of the rate of hydrodechlorination of chlorobenzene over the catalyst $Pd_3/PM2(B)$. Reaction conditions as in Table 3.

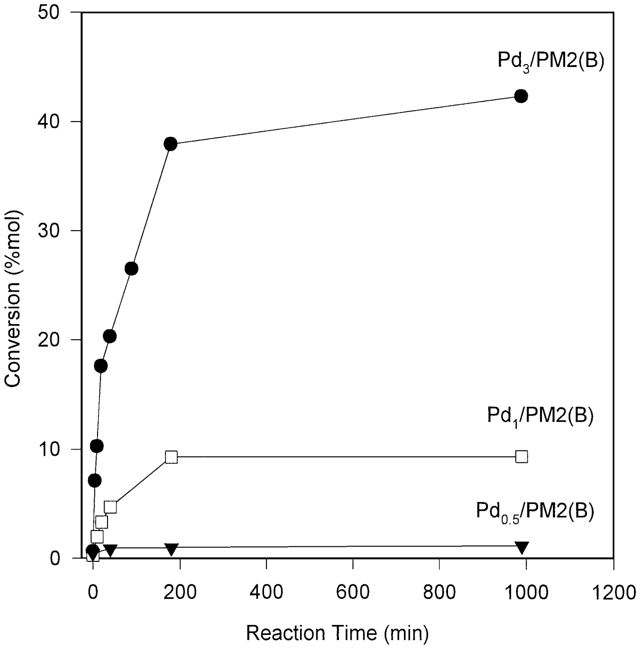

FIG. 2. Influence of the palladium content on the catalytic activity in the hydrodechlorination of chlorobenzene over palladium catalysts supported on solid PM2. Reaction conditions as in Table 3.

$Pd_{0.5}/PM2(B)$ to 42% for $Pd_3/PM2(B)$ (Table 3). In addition, this molar conversion was a residual value that was reached after a gradual decrease in catalytic activity. Some authors have ascribed this gradual decrease to the adsorption on metal palladium of a chloride ion released during the process (20, 21). This is consistent with our findings since the smaller the amount of Pd in the catalyst (the catalyst weight was always 100 mg), the sooner the catalyst was poisoned and the lower the residual conversion was. It is clear from these results that the poisoning is proportional to the overall metal surface area, at least at similar dispersions.

The initial specific rates (r_g) and TOF values were also very different. It is surprising that the Pd loading has such a big effect on the initial TOF values (Table 3). Nevertheless, we cannot discard the possibility that such values may be influenced by the poisoning effect of chlorine deposition. The TOF values were measured at conversion levels of about 1–5% where possible. However, for the $Pd_{0.5}/PM2(B)$ catalyst, the residual conversion was 1%. This seems to indicate that the TOF obtained is strongly influenced by the poisoning effect of chlorine and hence its very low value. However, the chlorine-poisoning effect should not affect the TOF values obtained in other catalysts for which the residual conversion value (X_{990}) is higher.

TABLE 3

Initial Activity (Specific Rate and TOF) and Residual Conversion at 990 min (X_{990}) in the Hydrodechlorination of Chlorobenzene over Palladium Catalysts Supported on Solid PM2

Catalyst	D (%)	d (A)	$r_g\ 10^2$ (mmol s^{-1} g_{Pd}^{-1})	TOF 10^2 (s^{-1})	X_{990} (%)
$Pd_{0.5}/PM2(B)$	33	34	3.3	1.1	1
$Pd_1/PM2(B)$	31	36	27.7	9.0	9
$Pd_3/PM2(B)$	26	43	71.8	29.8	42
$Pd_3/PM2(A)$	45	25	2.1	0.5	2
$Pd_3/PM2(Na)(B)$	54	21	10.6	2.1	10
$Pd_3/PM2(Na)(A)$	11	102	114	115	60

Influence of the Metal Precursor

The influence of the metal precursor used to prepare the catalysts can be inferred from the results shown in Table 3 for the catalyst obtained from palladium chloride, label (A) in the name, and palladium acetylacetonate, label (B). This effect can be analysed from two different points of view: the metallic dispersion obtained and the self-poisoning effect of chloride ions coming from the precursor.

Thus, the catalyst obtained from palladium chloride, $Pd_3/PM2(A)$, exhibited a higher metal dispersion (45%) than that prepared from palladium acetylacetonate, $Pd_3/PM2(B)$ (26%). In addition, this increased dispersion of the catalyst obtained from palladium chloride was associated with decreased initial activity in the hydrogenolysis of chlorobenzene (TOF $= 0.005\ s^{-1}$) and with residual conversion at 990 min, roughly 20 times lower than that obtained with the catalyst prepared from palladium acetylacetonate (2 and 42%, respectively). However, this difference in dispersion is not enough to account for the large difference seen in the initial activity and in the residual conversion, and thus it is reasonable to examine other contributory factors. On one hand, as stated above, the TOF values obtained for catalysts, for which the residual conversion value (X_{990}) is very low (i.e., Pd_3/PM2(A), $X_{990} = 2\%$), are supposed to be strongly influenced by the poisoning effect of chloride ions produced as the reaction proceeds.

On the other hand, the possible effect of the self-poisoning of the chloride ions coming from a $PdCl_2$ precursor in the case of the Pd_3/PM2(A) catalyst should be taken into account. To validate this fact, the Pd_3/PM2(B) catalyst, free of chloride ions coming from the metallic precursor, was exposed for 1 h at 393 K to a 50 ml min^{-1} 5% H_2/N_2 flow saturated with CH_2Cl_2. In this sense, the catalyst was poisoned by chloride ions, although we cannot underestimate the possibility that CH_2Cl_2 can also be a source of carbon (22, 23). EDX measurements of the treated catalyst detected chloride ions in a Cl/Pd molar ratio of 0.6. However, no signal corresponding to carbon was obtained by such a technique. The catalyst thus obtained was thereafter tested to measure the initial activity for chlorobenzene dehalogenation. The TOF obtained for the catalyst poisoned was 0.04 s^{-1}, significantly lower than that obtained for the catalyst free of chlorine ions (0.30 s^{-1}, Table 3). Moreover, the final conversion, X_{990}, was also significantly lower in this poisoned catalyst (15%) than in the nonpoisoned one (42%). These results indicate that the correct choice of the metallic precursor (free of chloride ions) is crucial for the optimum performance of the final solid obtained.

The effect of the metal precursor on catalytic activity also depends on other synthetic variables, as revealed by the results obtained from catalysts prepared by doping support PM2 with sodium, PM2(Na). This can be seen in Table 3 (entry 6), where the catalyst made from palladium chloride, Pd_3/PM2(Na)(A), exhibited a very low metal dispersion (11%) in addition to the highest initial catalytic activity (TOF = 1.15 s^{-1}) and residual conversion ($X_{990} = 60\%$). In this case, chloride ions coming from the palladium precursor do not deactivate the catalysts since they are associated with sodium atoms by forming NaCl, as detected by XRD.

On the basis of the previous results, the effect of the metal precursor on the resulting catalyst depends largely on other synthetic variables. Thus, palladium chloride leads to catalysts with widely variable dispersion and behaviour, depending on whether or not the support is previously doped with sodium. A similar conclusion can be drawn for the catalysts made from palladium acetylacetonate. Potential interactions between the precursor salts and the supports were not studied in this work, even though they are highly influential as they largely govern one of the principal properties of metal catalysts: their dispersion.

Influence of the Support

The role of the support in the hydrodehalogenation of organic halides has been analysed from various points of view (11, 20, 24–29). However, the acid–base properties of the support have never been considered in this context in an exhaustive manner.

Juszczyk *et al.* (24) examined, on one hand, the effect of the porous structure of the support on the dehydrochlorination of CFC-12 over Pd/Al_2O_3 and concluded that the catalytic activity was not affected by this factor, which, however, was found to influence the selectivity. On the other hand, the electronic state of the metal particles can be drastically modified by their interaction with electron-acceptor sites of the zeolite. Positively charged metal particles encaged in zeolites have been reported to exhibit higher catalytic activity toward hydrogenation (25).

Hydrophobic supports such as carbon have been found to have a favourable effect on this type of reaction by facilitating adsorption of the hydrophobic organic halide (26). The effect of the support has also been analysed in terms of the metal–support interface. In this respect, Coq *et al.* (20) and Juszczyk *et al.* (11), using Pd/Al_2O_3, suggested the migration of fluoride and chloride species from the metal to the interface to form halogenated species with the support, thereby refreshing the metal surface and avoiding the gradual passivation of the catalyst.

Finally, in close relationship to the foregoing, one must consider the potential influence of the acid–base properties of the support on the process. To the authors' minds, this is the most prominent factor when supports of rather different natures (e.g., ours) are to be compared. Schoonenboom *et al.* (28) studied the dechlorination of dioxins and furans over alumina supports with different acid–base properties and found basic supports to exhibit increased catalytic activity that they ascribed to the halogen atoms being captured by the basic sites of the alumina, which thus favoured their removal from the organic molecule.

To study the effect of our supports on catalytic activity and deactivation, we choose catalysts of similar metal dispersion, so as to minimize the effect of particle size, supported on such different solids as MgO, ZrO_2, and the $SiO_2/AlPO_4$ mixed system. Table 1 summarizes the textural and surface acid–base properties of the three supports. On one hand, as can be seen, PM2 was a solid with a high specific surface area, high surface acidity, and zero basicity. On the other hand, the MgO solid was essentially basic, even though it contained a residual amount of acid sites. Finally, the ZrO_2 support was an amphoteric solid of moderate acidity and basicity.

Table 4 shows the results provided by these catalytic systems. Regarding activity, the catalyst supported on MgO exhibited higher turnover frequencies than catalysts

TABLE 4

Initial Activity (TOF) and Residual Conversion at 990 min (X_{990}) in the Hydrodechorination of Chlorobenzene; Influence of the Support

Catalyst	D (%)	d (A)	$r_g\ 10^2$ (mmol s^{-1} g_{Pd}^{-1})	TOF 10^2 (s^{-1})	X_{990} (%)
$Pd_3/PM2(B)$	26	43	71.8	29.8	42
$Pd_3/MgO(B)$	33	34	162.2	53.1	31
$Pd_3/ZrO_2(B)$	36	31	25.8	7.6	56

supported on PM2 and ZrO_2 (see Fig. 3, which shows the activities of all the catalysts studied as a function of metal dispersion). This suggests that the textural and acid–base properties of the supports influence the specific activity of palladium-supported catalysts, which is not exclusively governed by the metal particle size (dispersion values are not very different).

Although the Pd/ZrO_2 catalysts, on one hand, was the least active in the reaction, it exhibited about a 50% conversion at 990 min; this can be ascribed to the chloride ion released in the reaction joining the support (presumably as zirconium oxychloride, $ZrOCl_2$) rather than anchoring itself to the metal surface, thereby avoiding passivation of the catalyst. However, XRD patterns provided no evidence of the presence of this species, so further research in this direction is needed.

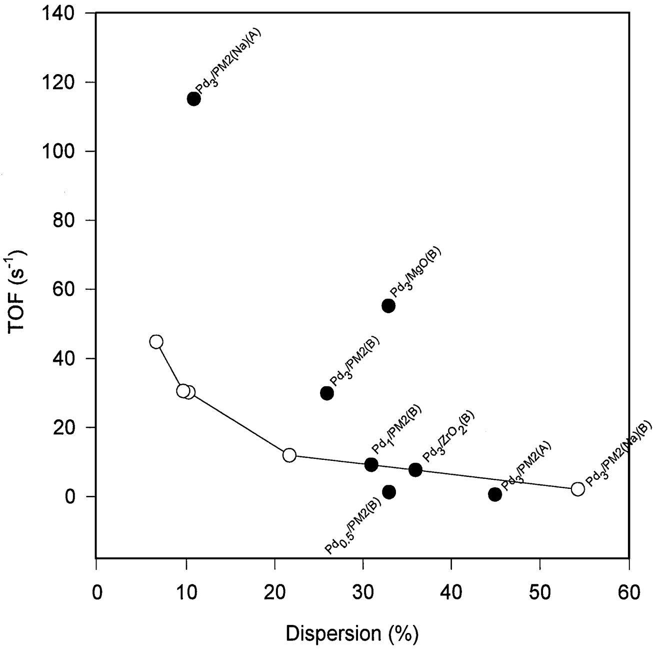

FIG. 3. Influence of metal dispersion on catalytic activity in the hydrodechlorination of chlorobenzene over different palladium-supported catalysts (●) (according to Table 3). Variation of the TOF in the hydrodechlorination of chlorobenzene against dispersion for the same catalyst ($Pd_3/PM2(Na)(B)$) reduced at different temperatures, in the 493–873 K range (○) (according to Table 5).

On the other hand, the Pd_3/MgO catalyst exhibited a low residual conversion (X_{990}). However, this support could be expected to capture chloride species similar to the ZrO_2 support, thus allowing the reaction to develop to a high conversion. Such a contradiction is only apparent since, after a given reaction time and, especially, at the acid pH resulting from the formation of HCl, the MgO support was dissolved. Choi *et al.* (27) previously observed this phenomenon (viz. a drastic drop in the specific surface area in a Pt/MgO catalyst), which they found to occur to a lesser extent, however, because their experiments were conducted in the gas phase. Also, these authors detected $MgCl_2$ in their XRD patterns (27).

Structure Sensitivity

There is no general consensus about the structure sensitivity of the hydrodehalogenation reaction on palladium catalysts (7–14). Thus, several authors working with different chlorinated compounds and palladium catalysts have found that an increase in dispersion caused the hydrodechlorination activity to fall (8, 10, 11). However, other authors (12–14) reported that the hydrodechlorination reaction is not sensitive to the structure of the catalysts.

A comparison of results reported in the literature is difficult to make. Reaction conditions, including gas- or liquid-phase reactions, catalyst support, reactants for which the hydrodechlorination is studied, etc., varied from one study to another, making it difficult to obtain a unified picture of the chemistry involved. Moreover, the inhibitory effect of HCl formed during the reaction also makes it difficult to compare data since, as a consequence of such inhibition, the turnover rate will be a strong function of conversion. In this regard, Ribeiro *et al.* (13, 14) took great care to obtain turnover rates free from the HCl inhibitory effect.

Our experimental findings suggest that the initial catalytic activity (TOF) is inversely related to metal dispersion (%D), as shown in Table 3. However, some of the catalyst tested had a different metallic precursor, supports, additives, etc. Differences in activity might have been caused by other contributory factors, rather than by a simple difference in dispersion values. To check the specific weight of those factors, several experiments were carried out starting from the catalyst $Pd_3/PM2(Na)(B)$, which had the highest dispersion (54%). This catalyst was treated in a H_2 flow (50 ml min^{-1}) at different temperatures (473–873 K) to obtain a catalyst with the same composition but with different dispersion values. These catalysts were tested for the hydrodehalogenation of chlorobenzene (Table 5 and Fig. 3). It was to be expected that as the catalyst reduction temperature increased, the dispersion obtained was lower. This decrease in the dispersion was accompanied by an increase in the catalyst activity (TOF) by a factor of 20. These

TABLE 5

Influence of the Reduction Temperature (T_r) in the Dispersion of Pd_3/PM2(Na)(B); Variation of the TOF and r_g in the Hydrodechlorination of Chlorobenzene

T_r (K)	D (%)	r_g 10^2 (mmol s^{-1} g_{Pd}^{-1})	TOF 10^2 (s^{-1})
493	54	10.6	2.1
573	22	24.1	11.8
673	10	27.6	30.1
723	9	27.8	30.5
873	7	28.1	44.7

differences in TOF values are hardly explicable, although different factors could be considered. As commented on above, the TOF values are strongly influenced by the inhibitory effect of HCl formed during reaction. Although TOFs are obtained from low conversion data (less than 5%), catalysts with a low residual conversion at 990 min (i.e., those suffering from severe poisoning, even at low conversion) could lead to unusually low TOF values. Moreover, the largest changes in the TOF values concern the low dispersion region (7–22%, Fig. 3), where neither structural nor electronic properties of Pd change much with the metal particle size. The high TOF value obtained for the catalyst reduced at 873 K (7% dispersion) is surprising in comparison to the catalyst reduced at 723 K (9% dispersion). An explanation could be the possible formation of the βPdH phase that should be stable at the reaction conditions. This hydride phase would be an alternative source of hydrogen that will make more reactive big palladium particles (βPdH formation) than small ones (no βPdH).

On the other hand, the dependence of the residual conversion at 990 min, X_{990}, on dispersion (see data in Table 3) suggests that the passivation or poisoning of palladium is also structure-sensitive. A better resistance against chlorine was observed when the size of the metallic particle increased, and thus, higher residual conversions were obtained for the less well-dispersed catalysts. These results seem to indicate that this inhibitory effect is not a surface phenomenon but rather one directly related to the bulk of the metal particle. Thus, since the catalysts that exhibited low dispersion (low metal surface areas and large particle sizes) and had low Pd_{surf}/Pd_{bulk} ratios provided very high residual conversions that can only be ascribed to the migration of chloride species into large particles, thereby refreshing the outer surface for further reaction. Conversely, small particles, with higher Pd_{surf}/Pd_{bulk} ratios, became saturated rapidly with chloride ions, which rapidly poisoned the catalyst surface and hence inhibited its activity. This is consistent with the findings of Coq *et al.* (20) who, based on XRD measurements, suggested that the passivation of palladium during the hydrogenolysis of CFCs was related to the diffusion of fluoride and chloride species into the metal particles.

CONCLUSIONS

The results obtained in the catalytic hydrogenolysis of chlorobenzene over various palladium-supported catalysts allow us to draw several interesting conclusions in regard to the influence of the operating conditions on the process, namely, the following:

(a) Under standard conditions, the hydrogenolysis of chlorobenzene takes place at a gradually decreasing rate through progressive poisoning of the active phase.

(b) The reaction seems to be structure-sensitive in regard to the initial activity. However, this apparent particle size effect is overshadowed by the inhibitory effect of HCl as well as by the influence of the support (see Pd_3/MgO(B)), additives (Pd_3/PM2(Na)(A)), and metallic precursor that make their contribution to the final activity of the catalyst.

(c) A better resistance to chlorine is observed when the size of the metallic particle increases and, thus, higher residual conversions were obtained for low-dispersed catalysts. This result seems to indicate that this inhibitory effect is not a surface phenomenon but one directly related to the bulk of the metal particle instead. Besides, support and additives also play an important role in this subject.

(d) The effect of the palladium content on the initial activity is of great importance. On one hand, the higher the palladium loading, the higher the TOF and residual conversion. On the other hand, the metal precursor used and its interaction with the support have a decisive influence on metal dispersion and hence on the initial catalytic activity. The interaction, however, has not been studied in-depth. The correct choice of the metallic precursor (free of chloride ions) is crucial for the optimum performance of the final solid obtained.

(e) On one hand, the supports studied, which possess different acid–base properties, exert a strong influence on the catalyst activity and deactivation. Thus, supports that can capture chloride species (e.g., ZrO_2) allow the reaction to finalise within relatively short times. On the other hand, the MgO support dissolves as the pH of the reaction medium lowers due to the effect of the HCl formed and the reaction ends prematurely.

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