

# Liquid-phase hydrodechlorination of chlorobenzene over palladium-supported catalysts

## Influence of HCl formation and NaOH addition

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### Abstract

The influence of HCl production and NaOH addition on catalytic activity in the liquid-phase hydrodechlorination of chlorobenzene over palladium-supported catalysts was studied. The rate of dehydrochlorination reaction falls with time owing to the poisoning effect of HCl gradually formed as by-product. A partial reaction order of  $-1$  in HCl was found over the concentration range 0.05–0.3 M. The addition of NaOH as a proton acceptor was found to have a favourable effect only with the most disperse catalysts—by contrast, the alkali had an adverse effect on the activity of the least disperse solids. © 2002 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Chlorinated hydrocarbons are hazardous pollutants contained in various waste oils and other organic liquids. They constitute one of the most important classes of organic pollutants by virtue of their environmental impact and toxic effects. Especially prominent among them in this respect are polychlorobiphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), chlorofluorocarbons (CFCs) and miscellaneous chlorinated solvents.

Disposal of organohalogenated pollutants usually relies on thermal or catalytic burning, gas-phase thermal or catalytic dehydrohalogenation, hydrodehalogenation or hydrogenolysis. Hydrodehalogenation is

the most widely endorsed and promising choice for the treatment and detoxification of organohalogen waste [1–3]. The process usually involves a thermal, catalytic or reactive procedure. Catalytic hydrodehalogenation has recently emerged as a promising non-destructive alternative technology by which chlorinated waste can be converted into products of commercial value. It is simple, safe and effective, and very often ensures regeneration of the initial raw material [4].

Of all Group VIII noble metals known for their C–Cl bond cleavage and hydrogenation ability, palladium is regarded as the best catalyst for selectively replacing chlorine atoms with hydrogen. It not only promotes bond cleavage but also affects the transition metal least markedly by the poisoning effect of halide ions released [5–7].

The catalytic hydrodehalogenation of organic compounds over palladium catalysts was recently reviewed

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[8]. Catalytic dehydrogenolysis suffers from the inhibitory effect of hydrogen halides produced during the process [8–11]. The drop in dechlorination activity has been associated in one instance to a loss of the supported active phase [12] and also to surface poisoning through the formation of metal chloride species [10,11].

Blocking of active sites by the hydrogen halide can be avoided by, e.g. using a base additive such as NaOH, NH<sub>3</sub>, etc. [8,12–16]; as a result, organic halides are usually hydrogenolysed in the presence of a base (especially in batch reactions). The role of the added base is to neutralize the acid and to keep the catalytic metal in a reduced state, free from halide ions. Sodium, potassium, calcium and barium hydroxides are usually employed for this purpose, as are sodium acetate, amines and ammonia for base-labile compounds.

Little research has so far been conducted, however, 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.

In this work, the deactivating effect of acid released during the reaction was examined. In addition, the effect of the addition of NaOH to the reaction medium in order to neutralize the HCl produced and prevent it from attacking the catalytic support was examined.

## 2. Experimental

### 2.1. Synthesis and characterization of catalysts

The support for the metal catalysts was a coprecipitated 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 support was described in detail in a previous paper [17]. 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 designated PM2(Na).

Both supports were used to prepare metal catalysts by depositing palladium using the incipient wetness impregnation method. The metal precursor was

either palladium chloride or palladium acetylacetonate (labels A and B, respectively, in the catalyst name). The support was placed in a flask that was supplied with an appropriate amount of metal precursor dissolved in acetone to reach a 3 wt.% palladium in the final catalyst, as denoted by the subscript. The flask was then placed in a rotavapor equipped with a water bath at 45 °C and spun for 6 h. Next, the solvent was evaporated in vacuo and the residue dried in a stove at 110–120 °C for 24 h, ground and sifted to a fine powder. Finally, the powder was calcined in an air stream (flow rate 50 ml min<sup>-1</sup>) by raising the temperature linearly to 300 °C and then holding it for 2 h.

With Pd<sub>3</sub>/PM2(A), two different portions of the catalyst were modified after palladium impregnation by adding NaOH and NaNO<sub>3</sub> aqueous solutions (basic and neutral, respectively). In both cases, an appropriate volume of solution was added to obtain a 5% sodium loading. The solids were calcined in the same way as the initial catalyst. The catalysts thus obtained were reduced in a hydrogen stream at a flow rate of 120 ml min<sup>-1</sup>. The reduction programme was started at 110 °C, which was held for 1 h and then raised to 200 °C linearly at 2 °C min<sup>-1</sup>, 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 thorough reduction of supported palladium in all systems.

The textural properties of the supports and metal catalysts were determined from nitrogen adsorption–desorption isotherms run at liquid nitrogen temperature on a Micromeritics ASAP 2000 instrument. Their specific surface areas (*S*<sub>BET</sub>) were obtained using the BET method.

The metal properties of the catalysts, viz mean metal particle size (*d*<sub>MET</sub>), metal surface area (*S*<sub>MET</sub>) and metal dispersion (*D*), were determined by hydrogen chemisorption at 100 °C on a Micromeritics TPD/TPR 2900 analyser (see Table 1).

### 2.2. Procedure

The liquid-phase hydrogenation of chlorobenzene with molecular hydrogen was carried out on a Parr Instruments 3911 low-pressure reactor, using a constant rate of 300 shakes min<sup>-1</sup>. The reaction vessel (volume 500 ml) was wrapped in a metal jacket

Table 1

Specific surface area ( $S_{\text{BET}}$ ) of the supports and specific surface area ( $S_{\text{BET}}$ ), mean metal particle diameter ( $d_{\text{MET}}$ ), metal surface area ( $S_{\text{MET}}$ ) and metal dispersion ( $D$ ) of the palladium-supported catalysts studied

Support		Metallic catalysts				
Name	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	Name	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{MET}}$ ( $\text{m}^2 \text{g}_{\text{Pd}}^{-1}$ )	$d_{\text{MET}}$ (Å)	$D$ (%)
PM2	413	Pd <sub>3</sub> /PM2(B)	387	114	43	26
		Pd <sub>3</sub> /PM2(A)	325	201	25	45
		Pd <sub>3</sub> /PM2(A)–NaOH	138	41	124	9
		Pd <sub>3</sub> /PM2(A)–NaNO <sub>3</sub>	298	188	27	42
PM2(Na)	272	Pd <sub>3</sub> /PM2(Na)(A)	192	50	102	11
		Pd <sub>3</sub> /PM2(Na)(B)	264	243	21	54

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

All reactions were conducted in a overall liquid volume of 20 ml containing 0.5 M chlorobenzene in methanol, using an initial hydrogen pressure of 0.414 MPa and a temperature of 40 °C.

Prior to each reaction, an amount of 100 mg of previously reduced metal catalyst was activated in a hydrogen stream at 120 ml min<sup>-1</sup> at 120 °C 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 activated catalyst. After the temperature levelled off at 40 °C, 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 catalyst 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 intraparticulate and interparticulate 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 intraparticulate diffusion [16]. The specific rate ( $\text{mmol s}^{-1} \text{g}_{\text{Pd}}^{-1}$ ) was found not to depend on the shaking rate above 200 shakes min<sup>-1</sup>. On the other

hand, it was 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 0.98 in each compound. This linear relationship suggests that the dehalogenation rate was kinetically controlled throughout the catalyst weight range studied [14]. The initial catalytic activity (TOF) was calculated at a chlorobenzene conversion lower than 5%. The chlorobenzene conversion at 990 min ( $X_{990}$ ) was determined in order to compare catalyst deactivation data.

### 2.3. 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. Supelcowax-10 semi-capillary column and fitted to an FID detector. Products were quantified using cyclohexane as internal standard.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The textural properties of the supports and catalysts were determined from nitrogen adsorption–desorption isotherms run at liquid nitrogen temperature (see Table 1).

The aggressive, NaOH-based treatment to which solid PM2 was subjected to obtain catalyst PM2(Na) resulted in a dramatic decrease in specific surface area (from 413 to 272  $\text{m}^2 \text{g}^{-1}$ ). The incorporation of palladium into the support caused an additional decrease, especially with PdCl<sub>2</sub> as precursor salt (compare the

Table 2  
Textural properties of PM2, PM2–0.3HCl and PM2–0.5HCl

Support	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	$V_{\text{p}}$ ( $\text{ml g}^{-1}$ ) <sup>b</sup>	$d_{\text{p}}$ ( $\text{Å}$ ) <sup>c</sup>
PM2	413	0.69	53
PM2–0.3HCl	419	0.67	50
PM2–0.5HCl	414	0.69	53

<sup>a</sup> Specific surface area ( $S_{\text{BET}}$ ).

<sup>b</sup> Cumulative pore volume ( $V_{\text{p}}$ ).

<sup>c</sup> Mean pore radius ( $d_{\text{p}}$ ).

data for PM2 and Pd<sub>3</sub>/PM2(A) on the one hand, and PM2(Na) and Pd<sub>3</sub>/PM2(Na)(A) on the other). One possible origin for this loss of surface area is degradation of the support at the acid pH of the PdCl<sub>2</sub> solution (dissolution of PdCl<sub>2</sub> requires the addition of HCl). This is consistent with the fact that impregnation with palladium acetylacetonate in acetone caused a much less substantial reduction in the surface area of the solid.

In order to check this hypothesis, the effect of the addition of high concentrations of HCl to the support—and hence to the final catalyst—was studied. Solid PM2 was treated with HCl, using the same procedure as for its synthesis—with the exception that the metal precursor was replaced with an HCl solution. Table 2 shows the textural properties of the support PM2, both in pure form and upon treatment with 0.3 and 0.5 M HCl. Obviously, the acid caused no change in the support's initial properties. Based on these results, the possibility of an acid solution of the PdCl<sub>2</sub> precursor substantially altering the textural properties of the resulting solid can be ruled out.

We also subjected the supports obtained by treating solid PM2 with HCl to EDX analysis in order to obtain information about its surface composition. The results (Table 3) reveal substantial changes in composition. Thus, increasing the HCl concentration decreased the surface content of phosphorus and aluminium, and increased that of silicon. This suggests that treating support PM2 with HCl redissolves some AlPO<sub>4</sub>, thereby enriching the solid surface with SiO<sub>2</sub> and decreasing the P/Si ratio. Taking into account that SiO<sub>2</sub> contributes the specific surface area and AlPO<sub>4</sub> the chemical textural properties of the solid, these results are consistent with the previous ones (Table 2) treating the solid with the acid scarcely alters its surface area. By contrast, its chemical surface properties must undergo substantial changes.

Table 3  
EDX analysis of PM2, PM2–0.3HCl and PM2–0.5HCl

Support	Element	Weight %	Atomic %
PM2	O	61.8	74.2
	Al	8.5	6.0
	Si	20.0	13.7
	P	9.5	5.9
	Na	0.2	0.2
	Cl	–	–
PM2–0.3HCl	O	56.5	69.7
	Al	6.7	4.9
	Si	28.9	20.3
	P	7.7	4.9
	Na	0.1	0.1
	Cl	0.07	0.04
PM2–0.5HCl	O	57.0	70.1
	Al	2.2	1.6
	Si	38.0	26.6
	P	2.5	1.6
	Na	0.05	0.04
	Cl	0.2	0.1

On the other hand, destruction of the catalyst's pore network through the thermal processes of calcination and reduction can also be discarded as these treatments were conducted at temperatures well below that of calcination of support PM2 (600 °C) [17].

Alternatively, the decrease in surface area may result from clogging of the pore network by deposited metal palladium. In this respect, the greater size of palladium acetylacetonate should result in adsorption/binding on the more readily accessible region of the solid surface (the outermost layer), which would cause no significant loss of surface area. The smaller size of palladium chloride may allow it to reach the smaller pores in the solid and clog them, thus significantly reducing the specific surface area.

In metal catalysts modified a posteriori with sodium salts, the effect of doping on textural properties depends to a great extent on the particular salt used. Thus, impregnation of catalyst Pd<sub>3</sub>/PM2(A) with NaNO<sub>3</sub> solution (at neutral pH) reduced the specific surface area of the final solid, Pd<sub>3</sub>/PM2(A)–NaNO<sub>3</sub>, only slightly. By contrast, impregnation with a markedly basic solution (NaOH) decreased the specific surface area by as much as 60%.

As regards metal dispersion, subsequent doping of catalyst Pd<sub>3</sub>/PM2(A) with NaOH reduced it

dramatically (from 45% to only 9%), possibly as a result of the aggressive treatment applied. In this respect, doping with a neutral salt such as  $\text{NaNO}_3$  caused no significant decrease in dispersion.

### 3.2. Hydrogenolysis of chlorobenzene

#### 3.2.1. Previous results

In the previous work [15,18], we reported on the liquid-phase hydrodehalogenation of chlorobenzene with molecular hydrogen over various palladium-supported catalysts. The results revealed that the catalysts were strongly deactivated by HCl formed during the reaction. Thus, the hydrogenolysis of chlorobenzene on catalyst  $\text{Pd}_3/\text{PM2(B)}$  was found to stop at 42% molar conversion to benzene, corresponding to a 0.21 M concentration of released HCl [18].

On the other hand, the catalysts prepared from chlorine-containing palladium precursors (e.g.  $\text{PdCl}_2$ ) were found to exhibit very low activity, presumably because palladium particles were deactivated by adsorption of chloride ions resulting from the decomposition of the metal precursor, as observed in catalyst  $\text{Pd}_3/\text{PM2(A)}$  [18]. However, when the support was doped with sodium, chloride ions from the precursor were captured by  $\text{Na}^+$  ions and the resulting catalysts exhibited increased activity in the hydrodehalogenation reaction as was the case with  $\text{Pd}_3/\text{PM2(A)}$  [15].

Also, in order to reduce the extent of deactivation of the catalyst, the effect of adding NaOH as a proton acceptor to the reaction medium was examined. The results, however, were inconclusive as, in most cases, the opposite effect was encountered: the addition of NaOH decreased the catalytic activity in the hydrodechlorination of chlorobenzene [15].

#### 3.2.2. Effect of HCl released in the reaction

In pioneering work, Campbell and Kembal [19] investigated the gas-phase dehalogenation of ethyl chloride on evaporated films of Pd, Pt and Ni, and noted the poisoning effect of HCl produced on the reaction rate. At present, there is general agreement that the activity of palladium metal-supported catalysts is inhibited by HX formed in the hydrodehalogenation of organic halides in both the gas [7,10,20–23] and the liquid phase [12,14,18,24]. However, batch processes suffer from the strong poisoning effect of HCl [25], while the use of reactants flowing through

a fixed bed reactor avoids local excesses of HCl on the catalyst [26]. This inhibitory effect of the reaction product, HCl, results in a negative reaction order (–1) as found by Somorjai and co-workers [21,27] working with model catalysts.

The negative effect of HCl may be a result of two essential factors. First, one must consider the competitive adsorption of HCl and the substrate to be reduced on palladium particles as found by Coq et al. [10] in the gas-phase hydrogenolysis of chlorobenzene. Second, the corrosive medium produced by the acid released may degrade the catalyst (both the support [24] and the metal phase [12]).

In order to acquire a deeper knowledge of the nature of this adverse effect, we examined the variation of the initial catalytic activity ( $r_g$  and TOF) of catalyst  $\text{Pd}_3/\text{PM2(B)}$  as a function of the concentration of HCl (0.05–0.8 M) added to the reaction medium. It should be noted that the highest concentration of HCl could reach following hydrogenolysis of 100% of the initial chlorobenzene was 0.5 M. Fig. 1 shows the results obtained.

Overall, the catalytic activity decreased gradually with increasing HCl concentration; the decrease was maximal at a 0.3 M concentration ( $r_g = 0.11$  vs.  $0.72 \text{ mmol s}^{-1} \text{ g}_{\text{Pd}}^{-1}$  with no HCl added). This result is consistent with the fact that the hydrodechlorination of chlorobenzene over  $\text{Pd}_3/\text{PM2(B)}$  when no

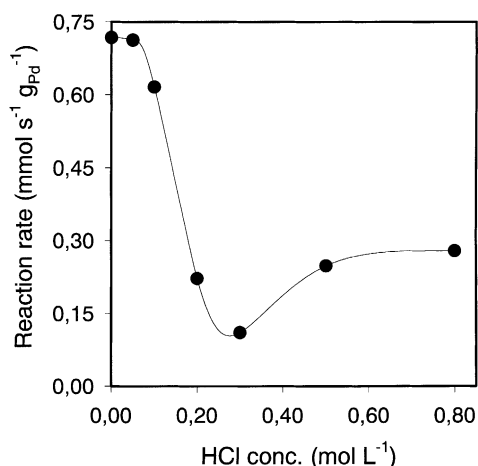


Fig. 1. Initial catalytic activity in the liquid-phase hydrogenolysis of chlorobenzene over  $\text{Pd}_3/\text{PM2(B)}$ . Influence of the amount of HCl added to the reaction mixture.

hydrochloric acid was added to the medium stopped at a benzene molar conversion of 42%, which corresponds to a released HCl concentration of 0.21 M [18]. At higher HCl concentrations (0.3–0.8 M), the catalytic activity remained constant at the levels found with a 0.2 M concentration of HCl. As noted earlier, however, some  $\text{AlPO}_4$  is redissolved under these conditions, which alters the surface chemical properties of the support and also, probably, causes some palladium to be dissolved as well.

The results obtained with low initial concentrations of HCl (0.05–0.3 M) allowed us to determine the reaction order in hydrochloric acid from the slope of a log–log plot of the initial reduction rate,  $r_g$ , against the HCl concentration over that interval. The reaction order thus obtained was  $-1$  and confirmed the inhibitory effect of HCl, consistent with previous results of other authors [10,21,23,27].

### 3.2.3. Effect of the addition of NaOH to the medium

One of the procedures usually employed to counter the adverse effects of the acid released during the reaction involves adding a base to the medium [12,14,16,18,24,28–30].

In our case, benzene was hydrogenolysed by adding NaOH in order to neutralize the hydrogen chloride produced and avoid deactivation of the catalyst. Thus, the reaction medium was supplied with the amount of base required to neutralize that of hydrogen chloride theoretically produced in the hydrogenolysis of the halide on the assumption of 100% conversion. Consequently, the reaction was conducted in a methanol solution containing a 0.5 M concentration of both NaOH and chlorobenzene. Table 4 shows the catalytic activity

Table 4

Influence of the NaOH addition on the initial catalytic activity (TOF) and conversion at 990 min ( $X_{990}$ ) in the chlorobenzene catalytic hydrodechlorination

Catalyst	0 M NaOH		0.5 M NaOH	
	TOF ( $\text{s}^{-1}$ )	$X_{990}$ (%)	TOF ( $\text{s}^{-1}$ )	$X_{990}$ (%)
$\text{Pd}_3/\text{PM2(B)}$	0.298	42	0.007	8
$\text{Pd}_3/\text{PM2(A)}$	0.005	2	0.005	13
$\text{Pd}_3/\text{PM2(Na)(B)}$	0.021	10	0.137	43
$\text{Pd}_3/\text{PM2(Na)(A)}$	1.150	60	0.064	5
$\text{Pd}_3/\text{PM2(A)-NaOH}$	0.114	13	0.067	5
$\text{Pd}_3/\text{PM2(A)-NaNO}_3$	0.010	25	0.237	17

(TOF) and conversion at 990 min ( $X_{990}$ ) obtained with the different catalysts in the presence and absence of sodium hydroxide.

Although adding a base to increase the final conversion in the hydrogenolysis of organic halides has been shown to have a favourable effect [14,16], our results reflect no unequivocal improvement in the initial catalytic activity (TOF) in the hydrogenolysis of chlorobenzene over PM2-supported palladium catalysts. Rather, the results for some catalysts reflect a detrimental effect; such an effect is especially marked on catalysts  $\text{Pd}_3/\text{PM2(B)}$  and  $\text{Pd}_3/\text{PM2(Na)(A)}$ , with which the reaction takes place at a considerably lower rate following addition of NaOH. By way of example, Fig. 2 illustrates the behaviour of catalyst  $\text{Pd}_3/\text{PM2(B)}$  in the presence and absence of a base.

Catalyst  $\text{Pd}_3/\text{PM2(A)}$  exhibited no effect as the solid was previously poisoned by chloride ions from the palladium precursor and had a very low TOF [18]. Other catalysts such as  $\text{Pd}_3/\text{PM2(Na)(B)}$  benefited from the addition of NaOH to the reaction medium and exhibited higher catalytic activity and conversion at 990 min as a result.

At this point, we chose two catalysts that reflected opposing responses to the addition of NaOH to the medium, viz  $\text{Pd}_3/\text{PM2(B)}$  (the catalytic activity of which decreased upon addition of the base) and  $\text{Pd}_3/\text{PM2(Na)(B)}$  (the activity and molar conversion

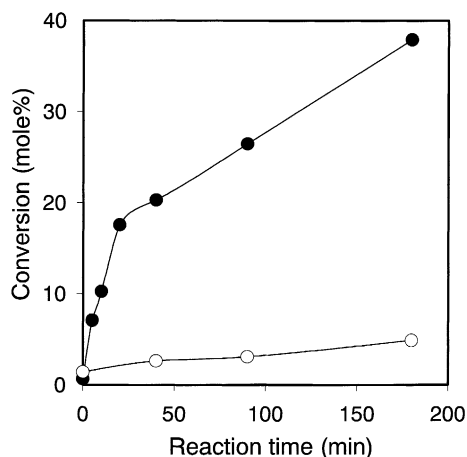


Fig. 2. Initial catalytic activity in the liquid-phase hydrogenolysis of chlorobenzene over  $\text{Pd}_3/\text{PM2(B)}$ . Influence of the NaOH (0.5 M) added to the reaction mixture. (●) MeOH; (○) MeOH/0.5 M NaOH.

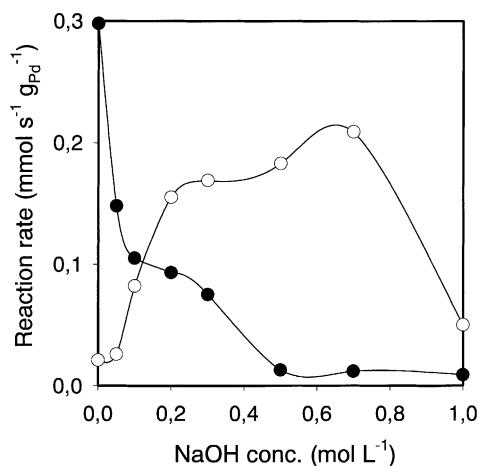


Fig. 3. Initial catalytic activity in the liquid-phase hydrogenolysis of chlorobenzene. Influence of the amount of NaOH (0.05–1 M) added to the reaction mixture, for catalysts Pd<sub>3</sub>/PM2(B) (●) and Pd<sub>3</sub>/PM2(Na)(B) (○).

of which were both increased by the added base). Both catalysts were examined in depth, using variable amounts of NaOH. Fig. 3 shows the variation of their catalytic activity upon addition of NaOH at a variable concentration (0.05–1 M) to the reaction medium.

As can be seen, the addition of NaOH to the reaction medium in the hydrogenolysis of chlorobenzene over catalyst Pd<sub>3</sub>/PM2(B) had an adverse effect, even at low concentrations of the base. Also, the effect on the initial catalytic activity increased with increasing concentration of NaOH (to a minimal residual value above a base concentration of 0.5 M).

With catalyst Pd<sub>3</sub>/PM2(Na)(B), the addition of NaOH to the reaction medium resulted in a gradual increase in catalytic activity up to a base concentration of 0.7 M, above which the initial rate exhibited the opposite trend.

Obviously, the addition of NaOH had a rather different effect on the two catalysts. Thus, high NaOH concentrations were seemingly detrimental to both, possibly as a result of the catalysts being degraded at the high prevailing pHs. Even more important—to our minds—, however, were the differences observed at low base concentrations. Thus, if sodium hydroxide plays its role as proton acceptor and neutralizes HCl released, then it will increase the catalytic activity—such was the case with Pd<sub>3</sub>/PM2(Na)(B). On the other hand, catalyst Pd<sub>3</sub>/PM2(B) exhibited no such increase

in activity, so the base either failed to capture HCl released or somehow inactivated or deteriorated the catalyst by itself. The more outstanding difference between the two catalysts was the presence of sodium in solid PM2, which constituted the support labelled PM2(Na). However, the catalysts exhibited one other crucial difference: their metal dispersion.

Fig. 4 shows the results of Table 4 in graphical form; the catalysts are arranged in increasing order of metal dispersion. Catalyst Pd<sub>3</sub>/PM2(A) is not included since, as noted earlier, it was poisoned by chloride ions from the metal precursor and exhibited very low catalytic activity as a result.

Fig. 4A shows the effect of NaOH added to the reaction medium on catalytic activity (TOF) in the hydrogenolysis of chlorobenzene. As can be seen, the base had an adverse effect on the catalysts with the lower metal dispersion (viz Pd<sub>3</sub>/PM2(A)–NaOH, Pd<sub>3</sub>/PM2(Na)(A) and Pd<sub>3</sub>/PM2(B)). By contrast, the catalysts with a metal dispersion above 40% (viz Pd<sub>3</sub>/PM2(A)–NaNO<sub>3</sub> and Pd<sub>3</sub>/PM2(Na)(B)) reflected a favourable effect of the addition of NaOH on their initial catalytic activity.

This behaviour is reflected in Fig. 3, which reveals that catalyst Pd<sub>3</sub>/PM2(Na)(B) (54% metal dispersion) required an NaOH concentration above 0.7 M to have its catalytic activity diminished, whereas catalyst Pd<sub>3</sub>/PM2(B) (26% metal dispersion) was subject to adverse effects from the presence of NaOH even at low concentrations.

The conversion at 990 min ( $X_{900}$ ) followed a very similar trend (see Fig. 4B). The most disperse catalyst (viz Pd<sub>3</sub>/PM2(Na)(B), 54% dispersion) reached substantially higher conversions in the presence of NaOH ( $X_{900} = 43\%$ ) than in its absence ( $X_{900} = 10\%$ ). On the other hand, catalyst Pd<sub>3</sub>/PM2(Na)(A) (11% dispersion) exhibited  $X_{900} = 5\%$  in the presence of NaOH and  $X_{900} = 60\%$  in its absence.

The base, therefore, seemingly has two opposing effects. Thus, its addition helps to keep the catalyst surface free of chloride ions, thereby avoiding poisoning of palladium particles. This effect is more obvious with small Pd particles. On the other hand, the base also has an adverse (possibly corrosive) effect that is particularly outstanding with the larger Pd particles.

These results suggests that the base affects catalytically active sites in a different manner depending on the size of the palladium particles. However, this is a

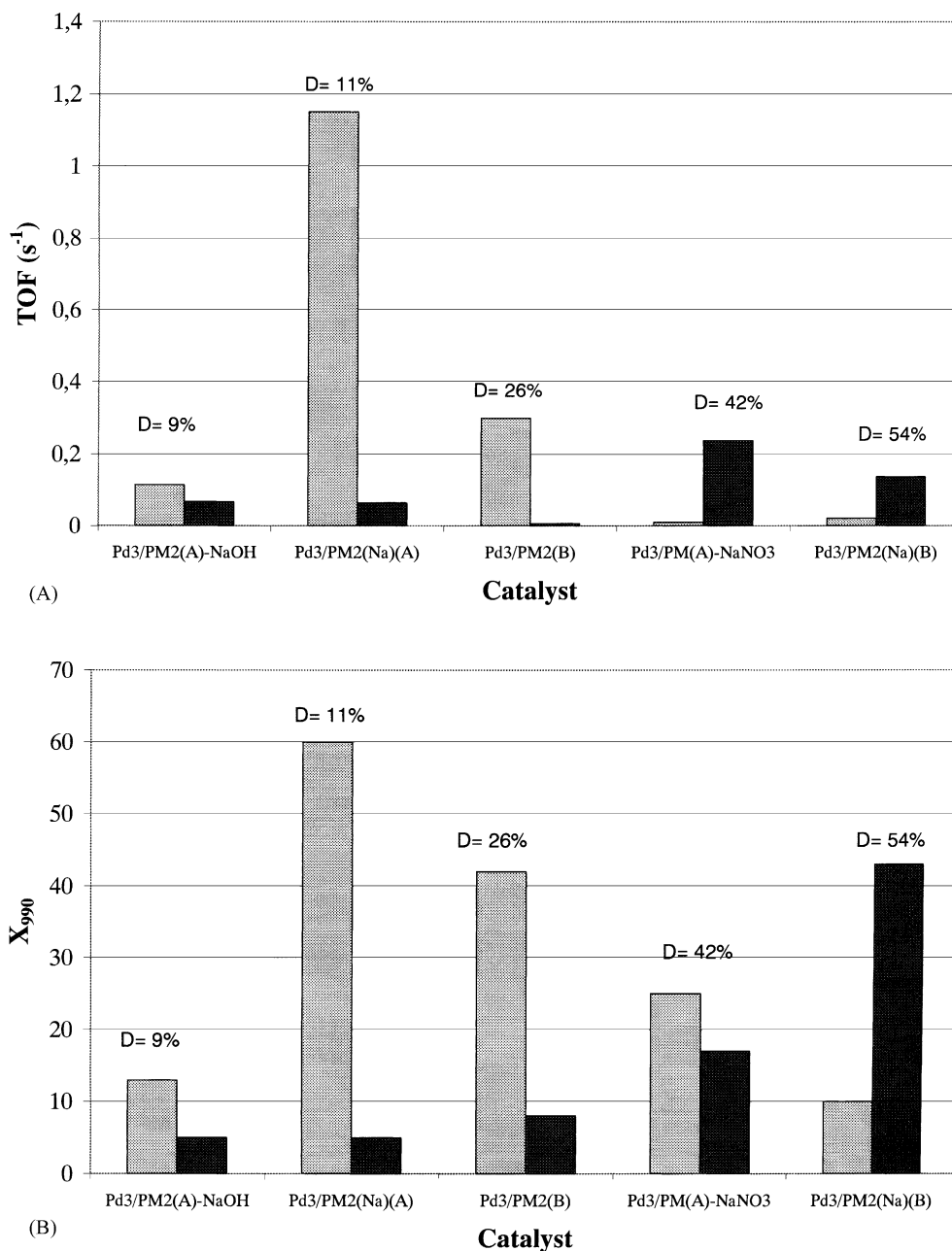


Fig. 4. Addition of NaOH in the liquid-phase hydrodechlorination of chlorobenzene. Influence on the initial activity (A) and conversion at 990 min,  $X_{990}$  (B).

general behaviour and no clear-cut mathematical relation appears to exist between the magnitude of the effect and the degree of dispersion of the catalyst. Further research is therefore required to clarify this

phenomenon. Specifically, it would be interesting to investigate similar trends in palladium catalysts supported on different solids and subjected to the action of bases of variable nature and strength.



#### 4. Conclusions

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

- (a) The rate of the reaction decreases as it develops through gradual poisoning of the catalysts by HCl formed during the process. This is confirmed by the reaction order with respect to HCl in the hydrodechlorination of chlorobenzene over catalyst Pd<sub>3</sub>/PM2(B) (−1).
- (b) The textural properties of the support, PM2, are not appreciably affected by the addition of HCl at the maximum working concentration used. However, the surface chemical properties can be altered through partial dissolution of AlPO<sub>4</sub> as the pH decreases.
- (c) The addition of NaOH to the reaction medium is intended to neutralize HCl formed during the reaction and hence to prevent it from poisoning the palladium. However, the effect of NaOH on the hydrogenolysis of chlorobenzene depends on the size of the palladium particles in the catalyst. Thus, scarcely dispersed catalysts (dispersion below 40%) do not benefit and highly dispersed ones benefit only slightly from the addition of the base. In any case, high concentrations of NaOH (e.g. 1 M) have adverse effects on all catalysts, possibly through corrosion of the support.

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