

# Structure and activity of microwave irradiated silica supported Pd–Fe bimetallic catalysts in the hydrodechlorination of chlorobenzene <sup>☆</sup>

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## Abstract

A series of silica supported Pd–Fe bimetallic catalysts were prepared by conventional as well as microwave heating methods. The catalysts were characterised by nitrogen adsorption (for BET surface area), X-ray diffraction (XRD), temperature-programmed reduction (TPR) and hydrogen chemisorption for their physico-chemical properties and were evaluated for chlorobenzene (CB) hydrodechlorination (HDC) activity. The catalysts prepared with microwave irradiation resulted into higher hydrodechlorination activity compared to their conventionally prepared analogues. These results are explained in terms of differences in the Pd morphology observed during the microwave irradiation. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Chlorobenzene; Hydrodechlorination; Pd–Fe bimetallic catalyst; Silica; Microwave irradiation

## 1. Introduction

Aromatic chlorocarbons are the most widespread and persistent toxic pollutants [1]. The disposal of these organic wastes is an important and difficult environmental problem. To date, incineration has largely been the preferred methodology for handling, or rather disposing of such organic waste and this process requires high destruction efficiency particularly when dealing with

halogenated aromatics [2]. Among the methods proposed for their destruction, catalytic hydrodechlorination (HDC) is of increasing interest because it excludes the formation of more toxic compounds such as dioxins and is applicable to treat waste with any content of chlorine particularly at low reaction temperatures [3–5].

The catalytic hydrodechlorination has been reported both in the gas and liquid phases using palladium [6,7], platinum [8], rhodium [6] and nickel [9] based catalysts. Palladium is the most active catalyst among all catalysts used for this reaction. The main problem associated with this reaction is the deactivation of the catalyst by HCl that is produced during the reaction [6]. However,

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the HDC activity of Pd was found to be affected by its particle size, the nature of the support and the extent of alloy formation when used with a second metal [7]. In this context, low dispersed Pd catalysts have been found to more resistant towards deactivation by HCl. Hence, the challenge is to prepare stable catalysts by adopting novel methods of preparation. Among various novel methods used in the preparation of catalysts, microwave irradiation is developing as effective technique offering rapid drying, moisture levelling, etc. [10]. Palladium, in combination with other noble or non-noble metal, is receiving attention as catalysts for the hydrodechlorination. In an earlier study on alumina-supported Pd–Fe catalysts prepared by microwave heating, we have observed higher activity in the HDC of chlorobenzene compared to the conventionally heated catalyst [11]. Silica, generally considered to be a weakly interacting support, is expected to offer a clear understanding of the change in morphology of Pd catalyst, subjected to microwave irradiation, and of the dependence of HDC activity on the morphology. The present study is an attempt in this direction.

## 2. Experimental

Supported Pd–Fe catalysts were prepared by impregnation on silica (Fluid silica, Ketjen, F-5; S.A: 640 m<sup>2</sup>/g; pore volume: 1.1 ml/g) with aqueous mixtures of Pd and Fe nitrate keeping the total composition of the active component of the catalyst at 10 wt% (metal). The catalysts were evaporated to near dryness on a water bath and further dried at 120 °C for 2 h in air. They were then divided into two portions. One portion of each catalyst was calcined in air at 450 °C for 5 h and the remaining portion was irradiated in a microwave oven (650 W power and 2.45 GHz frequency, CEM, USA) at 100% power for 5 min. X-ray diffraction (XRD) patterns were recorded on a Siemens D-5000 or a Phillips PW 1051 diffractometer using CuK<sub>α</sub> radiation. BET surface area was determined by nitrogen adsorption at –196 °C using an all-glass high vacuum apparatus. The same apparatus was used for the determination of hydrogen chemisorption capacities (at room tem-

perature) of catalysts reduced in hydrogen (at 250 °C, low temperature reduction (LTR) or at 525 °C, high temperature reduction (HTR)). The double isotherm method proposed by Benson et al. [12] and explained in detail by Bonivardi and Beltanas [13] was used to measure the chemisorbed amount of hydrogen. Temperature-programmed reduction (TPR) was performed using a 10% hydrogen 90% nitrogen gas mixture at a heating rate of 16 °C/min with a gas flow rate of 20 ml/min.

HDC of chlorobenzene was performed on catalysts prerduced in a flow of pure hydrogen at 250 or 525 °C, as the case may be. After bringing the reaction temperature to the required level (140–200 °C), chlorobenzene (3 ml/h) was fed by means of a microfeed pump (B. Braun, Germany) into the reactor in which the catalyst (8/25 BSS mesh, 0.8 g) was suspended between two quartz plugs. Purified hydrogen at a molar ratio of chlorobenzene:hydrogen equal to 1:3 was also admitted into the reactor. The liquid products were analysed by gas chromatography using a FID detector and a carbowax-20M column. The time on stream analyses carried out on these catalysts revealed that after 6 h the difference in two consecutive conversions was negligible. Hence, the product distribution after 6 h of reaction on stream was taken for the comparison of the performance of catalysts.

## 3. Results and discussion

The physical characteristics of the catalysts are presented in Table 1. The BET surface areas of the microwave irradiated catalysts are lower compared to their conventional counter parts. Under identical loading of active component the decrease in the surface area of the microwave treated catalysts could be attributed to increase in the particle size of Pd. The decrease in surface area normally observed with increase in active component loading is ascribed to decrease in micropore area due to pore filling.

The TPR profiles of the conventionally heated catalysts are shown in Fig. 1. The monometallic Fe catalyst (Fig. 1(a)) shows two temperature maxima at 420 and 620 °C which have been attributed to the two-stage reduction of Fe<sub>2</sub>O<sub>3</sub> to FeO through

Table 1  
Physical characteristics of silica supported mono and bimetallic Pd–Fe catalysts

Catalyst code	Pd (wt%)	Fe (wt%)	Pd/Fe atomic ratio	Surface area (m <sup>2</sup> /g)	
				Conventionally heated catalysts	Microwave irradiated catalysts
PFS-1	0	10	–	489	412
PFS-2	2.5	7.5	0.18	517	403
PFS-3	5.0	5.0	0.53	588	532
PFS-4	7.5	2.5	1.59	502	459
PFS-5	10	0	–	499	462

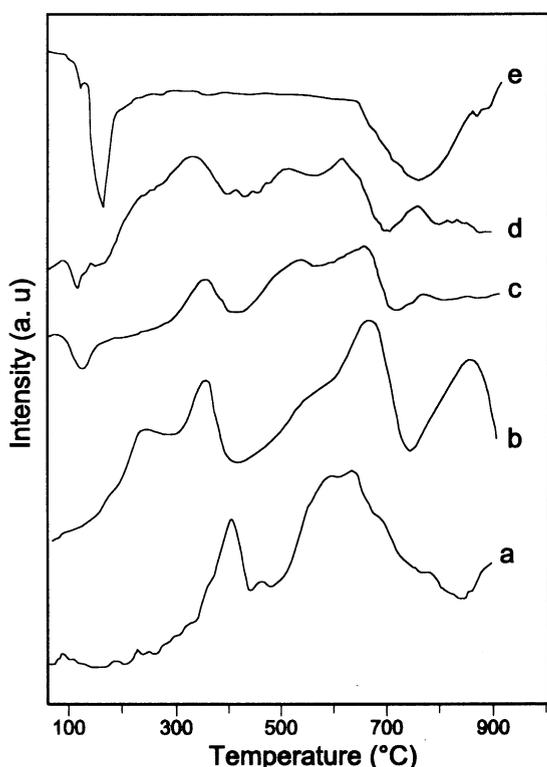


Fig. 1. TPR profiles of Pd–Fe/SiO<sub>2</sub> catalysts prepared by conventional heating method: (a) 10 wt% Fe (b) 7.5 wt% Fe, 2.5 wt% Pd, (c) 5 wt% Fe, 5 wt% Pd, (d) 2.5 wt% Fe, 7.5 wt% Pd, (e) 10 wt% Pd.

Fe<sub>3</sub>O<sub>4</sub>. The monometallic Pd catalyst shows (Fig. 1(e)) a negative peak, which can be attributed to hydrogen evolution due to decomposition of  $\beta$ -PdH phase. The TPR profiles of the bimetallic samples show a decrease in the temperature maxima when compared with the monometallic catalysts. In these profiles the negative peak is present

at higher Pd contents and disappears at higher Fe loading, which means that  $\beta$ -PdH phase formation is suppressed as the Fe content increases. This observation is well in concurrence with the earlier observations of Lietz et al. [14]. The higher the Pd content in bimetallic catalysts the more the reduction band of Fe<sub>2</sub>O<sub>3</sub> shifts to lower temperature and becomes less intense, suggesting strong interaction between Pd and Fe presumably leading to the alloy formation.

TPR patterns of the microwave treated catalysts are presented in Fig. 2. The reduction behaviour of monometallic catalysts is similar to that of conventionally prepared catalysts. Comparatively larger area of the desorption peak, in case of the monometallic Pd catalyst (Fig. 2(e)), gives an indirect evidence of the larger crystallite size leading to increased  $\beta$ -PdH formation.

The XRD profiles of the fresh catalysts prepared by conventional heating are shown in Fig. 3. These samples show a broad peak associated with silica, which indicates that it is poorly crystalline. The lines relating to PdO clearly indicate better crystallinity of PdO on silica, as also reported by Faudon et al. [15]. The monometallic Fe catalyst shows the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. The bimetallic catalysts show increasing intensities of the PdO with increasing Pd content.

The XRD patterns of the fresh catalysts prepared by microwave irradiation are shown in Fig. 4. In these catalysts better crystallinity is observed for monometallic Fe and Pd catalysts. Microwave irradiation thus seems to improve the crystallinity of the Fe and Pd oxides. The XRD analyses of the catalysts prepared by both methods after LTR are also carried out (figures not included). After LTR

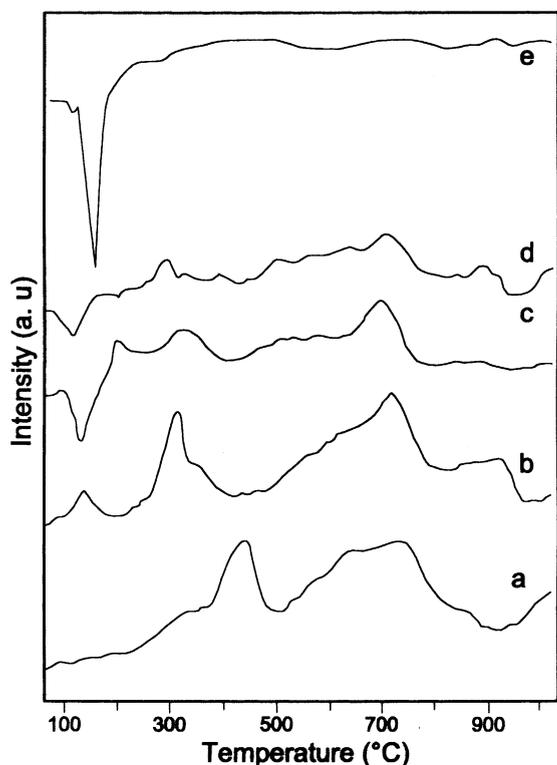


Fig. 2. TPR profiles of Pd-Fe/SiO<sub>2</sub> catalysts prepared by microwave irradiation method: (a) 10 wt% Fe, (b) 7.5 wt% Fe, 2.5 wt% Pd, (c) 5 wt% Fe, 5 wt% Pd, (d) 2.5 wt% Fe, 7.5 wt% Pd, (e) 10 wt% Pd.

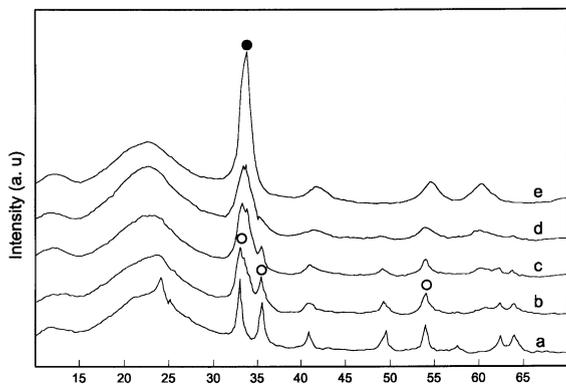


Fig. 3. XRD patterns of Pd-Fe/SiO<sub>2</sub> (fresh) catalysts prepared by conventional heating method: (a) 10 wt% Fe, (b) 7.5 wt% Fe, 2.5 wt% Pd, (c) 5 wt% Fe, 5 wt% Pd, (d) 2.5 wt% Fe, 7.5 wt% Pd, (e) 10 wt% Pd; (●) PdO; (○) Fe<sub>2</sub>O<sub>3</sub>.

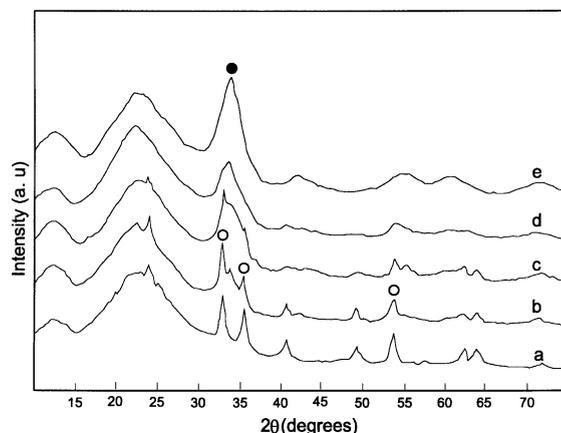


Fig. 4. XRD patterns of Pd-Fe/SiO<sub>2</sub> (fresh) catalysts prepared by microwave irradiation method: (a) 10 wt% Fe, (b) 7.5 wt% Fe, 2.5 wt% Pd, (c) 5 wt% Fe, 5 wt% Pd, (d) 2.5 wt% Fe, 7.5 wt% Pd, (e) 10 wt% Pd; (●) PdO; (○) Fe<sub>2</sub>O<sub>3</sub>.

the catalysts show similar patterns to that of fresh catalysts except the reduction of PdO to  $\alpha$ -Pd.

The XRD results of both the catalysts prepared by conventional and microwave irradiation after HTR treatment are summarised in Table 3. HTR appears to produce  $\alpha$ -Fe in the monometallic Fe catalyst and its appearance diminishes upon increase in Pd content. In monometallic Pd catalyst considerable formation of  $\alpha$ -Pd is noticed. All the bimetallic catalysts show peaks, which are related to Pd-Fe alloy. Pinna et al. [16] have reported the XRD patterns of the Pd-Fe/SiO<sub>2</sub> and observed a shift in the  $2\theta$  value of  $\alpha$ -Pd peak by about 0.2°. This shift in the peak is related to Pd-Fe alloy phase. Similar behaviour is also observed in the present investigation. The diffraction patterns of microwave heated catalysts are similar to those of their conventionally heated counterparts except the formation of Pd-Fe alloy.

The chemisorption uptakes after low and HTR of the catalysts prepared by conventional and microwave heating are presented in Table 2. The H<sub>2</sub> chemisorption data on Pd-Fe bimetallic system are difficult to be interpreted because of alloy and  $\beta$ -PdH formation. The H/Pd ratio also varies with Pd dispersion as reported by Bonivardi and Beltanas [13]. Hence it is difficult to accurately estimate the dispersion as well as the particle size based on hydrogen chemisorption data. However,

Table 2  
Hydrogen chemisorption data of silica supported Pd–Fe bimetallic catalysts after LTR and HTR

Catalyst code	Conventionally heated catalysts chemisorption ( $\mu\text{mol/g cat}$ ) at		Microwave irradiated catalysts chemisorption ( $\mu\text{mol/g cat}$ ) at	
	LTR	HTR	LTR	HTR
FPS-1	44.6	55.7	22.3	50.2
FPS-2	52	44	51.7	44.3
FPS-3	59.8	44.6	78.1	63.2
FPS-4	62.9	40.7	67.1	59.7
FPS-5	156	96.6	89.2	67

Table 3  
XRD results of the catalysts after HTR

Catalysts	XRD peaks					
	Conventionally heated catalysts			Microwave irradiated catalysts		
	Major peak	Medium peak	Minor peak	Major peak	Medium peak	Minor peak
FPS-1	$\alpha\text{-Fe}$	–	–	$\alpha\text{-Fe}$	–	–
FPS-2	$\alpha\text{-Pd}$	$\alpha\text{-Fe}$	–	$\alpha\text{-Pd}$	$\alpha\text{-Fe}$	–
FPS-3	$\alpha\text{-Pd}$	Pd–Fe alloy	$\alpha\text{-Fe}$	$\alpha\text{-Pd}$	$\alpha\text{-Fe}$	–
FPS-4	Pd–Fe alloy	$\alpha\text{-Pd}$	–	$\alpha\text{-Pd}$	–	$\alpha\text{-Fe}$
FPS-5	$\alpha\text{-Pd}$	–	–	$\alpha\text{-Pd}$	–	–

a comparative discussion can be made between the adsorption capacities of these catalysts. The chemisorption uptakes are calculated by assuming H/Pd as 1. Conventionally heated LTR-bimetallic catalysts show that upon the addition of 2.5 wt% Pd to Fe the hydrogen uptake increases. With further increase in Pd content, the  $\text{H}_2$  uptake is increasing continuously. Hydrogen uptake of the monometallic Pd catalysts after LTR records a high value possibly due to the easy reducibility of Pd before 250 °C.

In the case of HTR-conventionally heated catalysts the  $\text{H}_2$  uptakes are lower than the corresponding LTR catalysts except in case of monometallic iron catalyst. This decreased uptake in bimetallic catalysts may be due to the formation of Pd–Fe alloy. XRD and TPR patterns of these catalysts are in support of this observation. There is a marginal decrease in the chemisorption of HTR monometallic Pd catalyst compared to its LTR counterpart. Pd is more sensitive to heat treatment and hence might have undergone sintering after the HTR treatment.

The LTR microwave treated catalysts show similar trend as observed in the case of the conventionally heated catalysts. The monometallic Pd catalyst shows a lower chemisorption value than its conventional counterpart. It is known that the microwave irradiation leads to increase in particle size [17]. The HTR catalysts show a decrease in chemisorption value when compared to LTR catalysts with higher Pd content. However, these chemisorption values are relatively higher than those of HTR conventionally heated catalysts. The reason may be due to the absence of alloy formation in case of the MW catalysts, as it is evidenced by XRD.

HDC of chlorobenzene on mono- and bimetallic silica supported Pd–Fe catalysts between 140 and 200 °C resulted into the formation of benzene as the only product. The activity profiles of the catalysts after LTR are shown in Fig. 5(a). In the range of reaction temperature studied, the monometallic Pd shown the highest activity. Replacement of 2.5 wt% of Pd with Fe results into a substantial decrease in chlorobenzene conversion.

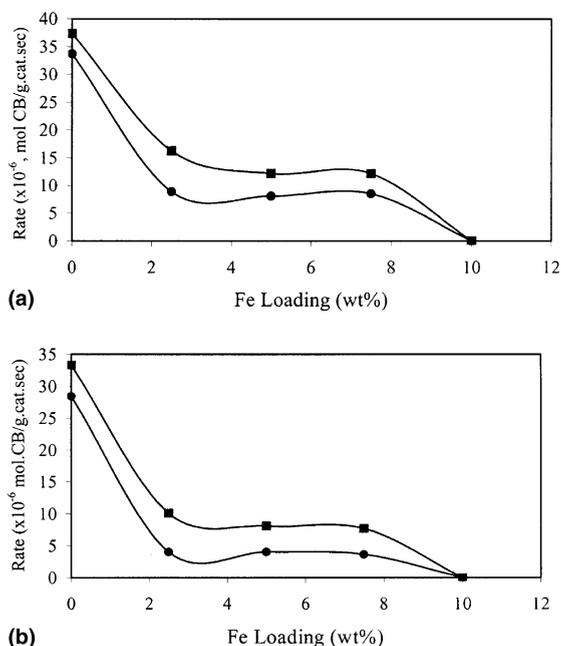


Fig. 5. Hydrodechlorination of chlorobenzene activity patterns of the Pd–Fe/SiO<sub>2</sub> catalysts prepared by conventional (CH) and microwave irradiation (MH) method after (a) LTR and (b) HTR (reaction temperature: 140 °C); (●) conventionally heated catalysts; (■) microwave irradiated catalysts.

However, further addition of Fe has no effect on the activity. Monometallic Fe has no activity for chlorobenzene conversion.

The catalysts treated with microwave irradiation have a higher activity when compared to the corresponding conventionally heated catalyst. The decrease in the conversion with the increase in Fe content may be due to dilution of the most active Pd. The higher activity in case of microwave treated catalysts can be explained in terms of particle size. In the HDC reaction, the particle size of the catalyst plays a significant role as reported by Coq et al. [6]; larger Pd particles are more active. For the sake of comparison we estimated the particle size of monometallic Pd catalysts prepared by both methods. The microwave treated catalyst has a average higher particle size (60 Å) than the conventional catalyst particle size (33 Å).

Fig. 5(b) shows the activity patterns of the HTR catalysts. HTR decreased the difference in activity

between the conventionally heated and microwave irradiated bimetallic catalysts when compared to the corresponding LTR catalysts. An important feature of the activity patterns of the bimetallic catalysts is that the activity is decreased considerably. Formation of Pd–Fe alloy after the HTR was observed from the XRD patterns of conventionally heated catalysts. Weaker salt support interaction on silica also makes the alloy formation very facile. Alloying of Pd with Fe induces a decrease in activity for the C–Cl hydrogenolysis, which can be understood as a decrease of the reducibility in the surface by hydrogen as evidenced by lower chemisorption values.

#### 4. Conclusions

Microwave irradiation enhanced the chlorobenzene conversion levels compared to the conventionally heated catalysts. Addition of Fe to Pd decreases the activity possibly by diluting the Pd or by forming the Pd–Fe alloy. Microwave irradiation appears to increase the Pd particle size and decrease the alloy formation thus retaining the activity. Silica offers a clean understanding of the change in morphology of the active species.

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