

Microwave heating during catalyst preparation: influence on the hydrodechlorination activity of alumina-supported palladium–iron bimetallic catalysts

F.J. Berry^a, L.E. Smart^{a,*}, P.S. Sai Prasad^{b,1}, N. Lingaiah^b, P. Kanta Rao^b

^a Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

^b Catalysis Section, Physical and Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 25 August 1999; received in revised form 3 March 2000; accepted 3 March 2000

Abstract

Alumina-supported Pd–Fe mono- and bimetallic catalysts have been prepared by microwave irradiation and by conventional calcination methods. The catalysts were characterised by powder X-ray diffraction (XRD), temperature-programmed reduction (TPR) and nitrogen adsorption measurements. Hydrogen chemisorption measurements were performed after low- and high-temperature reduction (LTR and HTR) of the catalyst. Hydrodechlorination of chlorobenzene was carried out on the reduced catalysts. Microwave heating changed the crystallite size and the susceptibility of the catalysts to alloy formation, with a resultant increase in the activity of the reduced catalysts for the hydrodechlorination of chlorobenzene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Microwave heating; Alumina-supported catalysts; Hydrodechlorination activity; Bimetallic catalysts

1. Introduction

Microwaves have been found to be useful in organic synthesis, material processing and waste remediation. Microwave radiation with a frequency ranging from 0.3 to 300 GHz (corresponding to a wavelength of 1 m to 1 mm) when applied to materials makes the dipolar molecules rotate and the ions migrate. The energy absorbed is dissipated as heat. Microwave heating is therefore internal as compared to conventional heat-

ing which is external. Thus, the application of microwaves, which causes rapid and even heating, opens up new opportunities in chemistry, materials science and other areas [1]. Microwave heating is now developing as an effective method for the preparation of catalysts [2,31] and can provide (i) rapid drying, (ii) moisture levelling leading to a uniform distribution of metal in the support, (iii) physically strong pellets compared to conventionally heated catalysts, and (iv) a change in the activity of the catalyst compared to its conventionally prepared analogues [3]. Microwave heating thus offers the possibility of developing catalysts with uniform pellet strength and enhanced reaction rates and selectivities.

The disposal of halogenated organic wastes [4] as well as chlorofluorocarbons [5] is an important environmental problem. Selective catalytic hydrogenolysis

* Corresponding author.

¹ Also corresponding author.

E-mail addresses: f.j.berry@open.ac.uk (F.J. Berry), l.e.smart@open.ac.uk (L.E. Smart), saiprasad@iict.ap.nic.in (P.S. Sai Prasad), saiprasad@iict.ap.nic.in (N. Lingaiah), saiprasad@iict.ap.nic.in (P. Kanta Rao).

has been recognised as an attractive alternative to various methods of destruction, such as incineration and chemical degradation [6]. Noble metals, particularly Pd [7], have been identified as promising catalysts for the selective cleavage of C–Cl bonds under mild conditions. The addition of metals such as Fe, Co or K can influence the selectivity to the hydrodechlorinated product [8], depending upon the composition of the feed in the hydrodechlorination of CCl_2F_2 to CH_2F_2 . It is known that the hydrodechlorination activity is affected by Pd particle size, nature of the support [9] and the extent of alloy formation under reducing conditions [10,11,32]. The effects of such changes in the catalyst and the extent of alloy formation with the method of preparation have not been studied. The transformation of CCl_2F_2 (CFC-12), a potentially hazardous chlorofluorocarbon associated with ozone depletion, into CH_2F_2 , has been the subject of several studies [12–14]. The work has sought to explain the synergic effects of well-mixed bi- or multimetallic catalysts. It has been noted that poorly dispersed Pd catalysts are more active [14] for this hydrodechlorination reaction, and also [15] that alloying Pd with Re has a detrimental effect on the catalytic activity for CCl_2F_2 reduction. We were interested in seeing if similar effects would be observed in the dechlorination of chlorobenzene, and thus, have sought to prepare bimetallic Pd catalysts for comparison.

In an earlier publication [3], we reported that microwave irradiation improves the turn over numbers during the hydrogenation of benzene on Pd supported on alumina and silica. Here, we report on our studies of alumina-supported Pd–Fe bimetallic catalysts prepared both by conventional heating and microwave irradiation techniques and the influence of particle size and alloy formation on the activity and selectivity of the catalysts during the hydrodechlorination of chlorobenzene.

2. Experimental

A series of alumina-supported mono- and bimetallic Pd–Fe catalysts were prepared by the impregnation of γ -alumina (Harshaw, Al-3996 R, crushed and sieved to 18/25 BSS mesh, SA=178 m²/g) with appropriate amounts of aqueous palladium nitrate (Aldrich) and iron(III) nitrate (Loba Chemie, India, GR grade) by

a simultaneous wet impregnation method. The catalysts were evaporated to dryness on a water bath and dried at 120°C (12 h) in air. A portion of each catalyst was calcined in air at 450°C (5 h) (hereafter denoted CH) and the remaining portion was irradiated in a microwave oven (CEM Corporation, USA) at 100% power (650 W, 5 min) (hereafter denoted MW). Each catalyst contained a total metal loading of 10 wt.% with Pd/Fe ratios varying between 0 and 1 (by weight of the metal).

Powder X-ray diffraction patterns (XRD) of the fresh catalysts were obtained with a Siemens D-5000 X-ray diffractometer and those of the reduced samples were obtained with a Phillips 1051 diffractometer using Cu K α radiation.

BET surface area measurements were determined by nitrogen adsorption at –196°C using a conventional all-glass high-vacuum unit. The same apparatus was also used to determine the room temperature hydrogen chemisorption capacities of the catalysts reduced in hydrogen at 250°C (low-temperature reduction (LTR)) and at 525°C (high-temperature reduction (HTR)) using the double isotherm method proposed by Benson et al. [16] and modified by Bonivardi and Baltanas [17], taking due consideration of possible hydride formation.

Temperature-programmed reduction (TPR) was performed using a 10% hydrogen–90% argon gas mixture at flow rate of 20 ml/min and a heating rate of 16°C/min in the temperature range 30–1100°C.

The chlorobenzene hydrodechlorination activity was evaluated on catalysts (approx. 0.4 g) prereduced (250 or 525°C) in a flow of pure hydrogen (30 ml/min, 4 h). The reaction was performed in the temperature range 140–200°C at atmospheric pressure. Chlorobenzene (SRL, India Analar grade) was fed at a liquid flow rate of 3 ml/h by means of a micro feed pump (Braun Corp., Germany) into a fixed bed tubular reactor in which the catalyst (18/25 BSS mesh, 0.8 g) was suspended between two quartz plugs. Purified hydrogen at a molar flow ratio of chlorobenzene:hydrogen equal to 1:3 was admitted into the preheater zone of the reactor. The time-on-stream analyses, carried out on the catalysts for 16 h, revealed negligible decrease in conversion after 6 h. The products were collected after 6 h of reaction on stream and analysed by gas chromatography using a FID detector and a 10% Carbowax 20M column (1/8 in. diameter; 8 ft length).

3. Results and discussion

TPR profiles of the conventionally heated catalysts are shown in Fig. 1 and those of the microwave-irradiated catalysts in Fig. 2. On account of the ability of palladium to adsorb hydrogen, quantitative comparisons of the amounts of hydrogen consumed in these experiments are not informative in terms of determining the state of reduction of palladium; however, useful inferences can be made from the temperatures at which reduction takes place and the presence or otherwise of β -palladium hydride. The TPR profile of the monometallic Al_2O_3 -supported Pd catalyst (CH) shows a feature at 144°C (Fig. 1e) which we associate with the liberation of hydrogen resulting from the decomposition of β -palladium hydride [3,10,32]. (It should be noted that the Pd on the

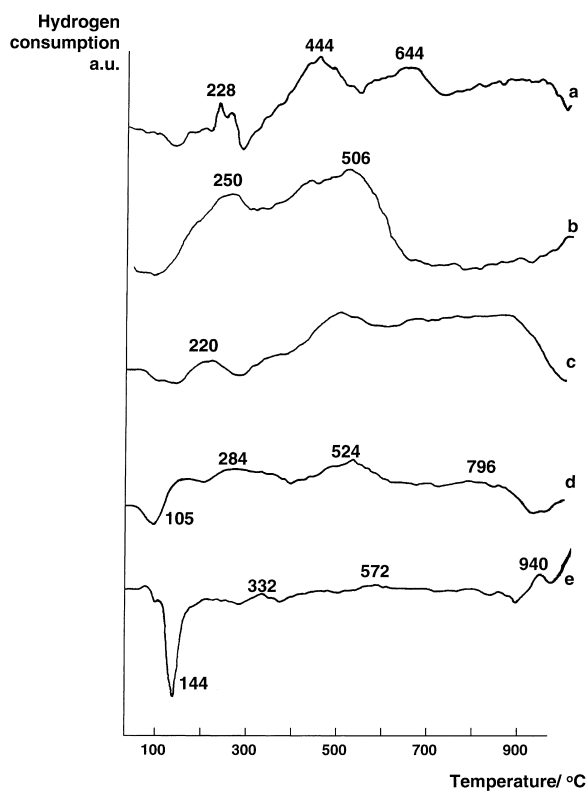


Fig. 1. The TPR profiles of Fe-Pd/Al₂O₃ catalysts prepared by conventional heating (CH): (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd.

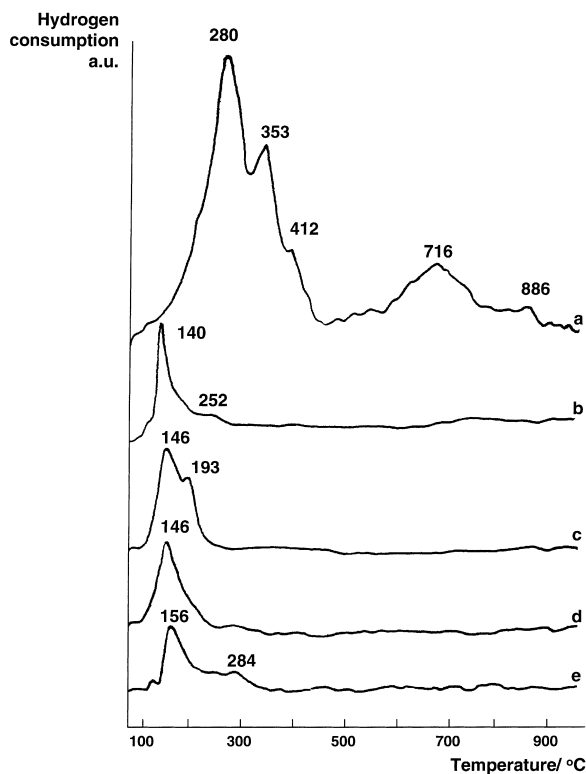


Fig. 2. The TPR profiles of Fe-Pd/Al₂O₃ catalysts prepared by microwave irradiation (MW): (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd.

alumina support is oxidised to PdO by calcination at 450°C . However, this is reduced to β -palladium hydride when the TPR apparatus is flushed with the H_2/N_2 mixture at room temperature before the start of each experiment. This reduction is sometimes very facile and has been observed at temperatures as low as ca. 270 K [10,32].) The TPR profile from the monometallic Al_2O_3 -supported Fe catalyst (CH) (Fig. 1a) shows that the reduction of Fe(III) to Fe(0) occurs at temperatures similar to those reported for the physical mixture of Fe_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ [18–20] (peaks observed at ca. 440 and 640°C correspond to those reported previously at ca. 470 and 630°C). The facile reduction of iron oxide in the presence of noble metals is well documented [21] and we observe this trend for all three bimetallic Pd-Fe catalysts (Fig. 1b–d) where the 640°C reduction peak is seen to shift to ca. 510°C . Catalysts with more than 50%

Pd prepared by conventional heating (Fig. 1c–e) all show a peak associated with the liberation of hydrogen from the formation of β -palladium hydride at low temperatures (144°C and below). This feature decreases in intensity as the iron content increases.

In Fig. 2a, the monometallic Fe catalyst (MW) displays a two-stage reduction of Fe(III) to Fe(0) presumably through Fe(II) or a mixture of Fe(III) and Fe(II) [18–20] with peak maxima at 280, 353 and 716°C. The monometallic Pd catalyst (Fig. 2e) exhibits a peak at 156°C in the TPR profile which we associate with the reduction of Pd(II) to Pd(0). The Pd–Fe bimetallic catalysts (Fig. 2b–d) show reduction features at significantly lower temperatures than the monometallic Fe catalyst (Fig. 2a). In the case of these catalysts, the main reduction takes place at temperatures below 150°C, suggesting that initial reduction to metallic Pd facilitates dissociative chemisorption of H₂ which is capable of reducing the ferric species at much lower temperatures than normally expected.

The XRD patterns of the unreduced MW catalysts and CH catalysts are shown in Figs. 3 and

4, respectively. Peaks due to PdO are in evidence in both monometallic catalysts (2θ 33.9, 54.8, ca. 60.5°). From the relative width of the peaks, it can be noted that the size of the PdO particles is slightly bigger for the CH catalyst compared to the MW catalyst. By contrast, the pattern of the monometallic Fe MW catalyst shows enhanced crystallinity for α -Fe₂O₃.

The XRD patterns of LTR and HTR microwave-irradiated catalysts are shown in Figs. 5 and 6, respectively. Neither catalyst showed evidence for the presence of PdO, but XRD does indicate the presence of a small amount of α -Fe₂O₃ in the monometallic Fe catalyst (Fig. 5a). In the HTR catalysts, the line corresponding to metallic Fe (2θ 44.7°) in the case of catalysts with high Fe content is observed. This agrees with TPR data suggesting a more facile reduction of α -Fe₂O₃ in the presence of Pd. There is evidence for the presence of Pd in the monometallic and high Pd-content catalysts, but there is no evidence for alloy formation in these bimetallic catalysts (Fe–Pd, 2θ 41.2 and ca. 48°) *vide infra*.

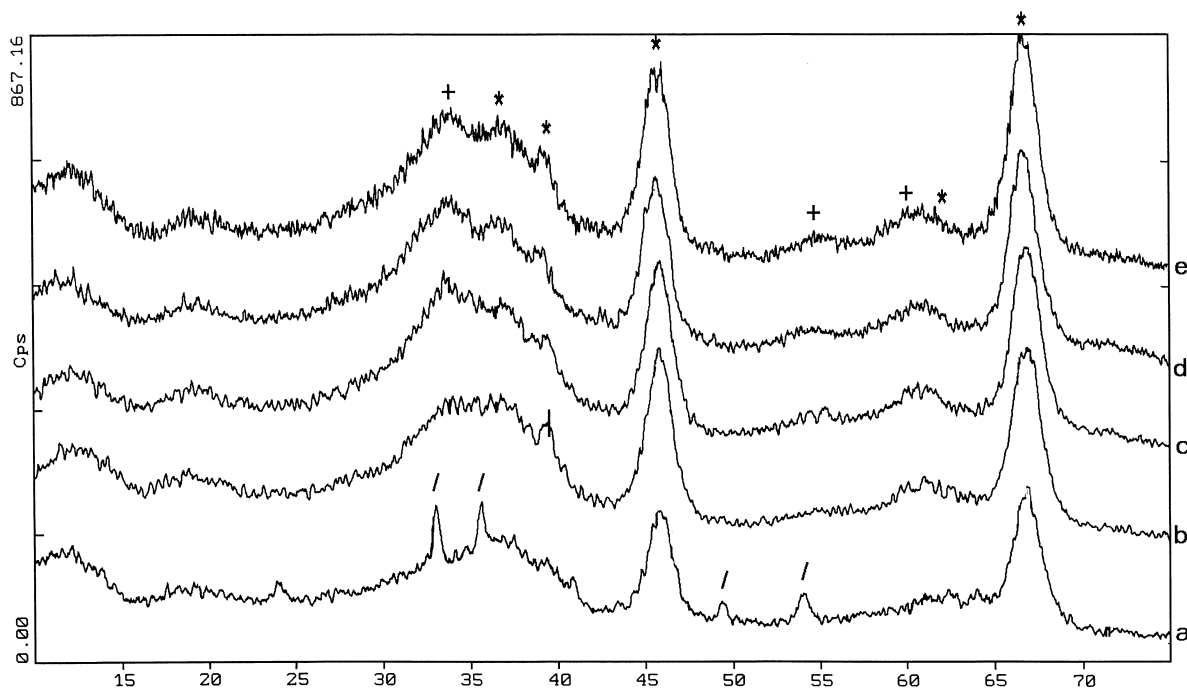


Fig. 3. XRD patterns of Fe–Pd/Al₂O₃ catalysts (unreduced) prepared by microwave irradiation (MW): (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd. PdO (+); γ -Al₂O₃ (*); α -Fe₂O₃ (/).

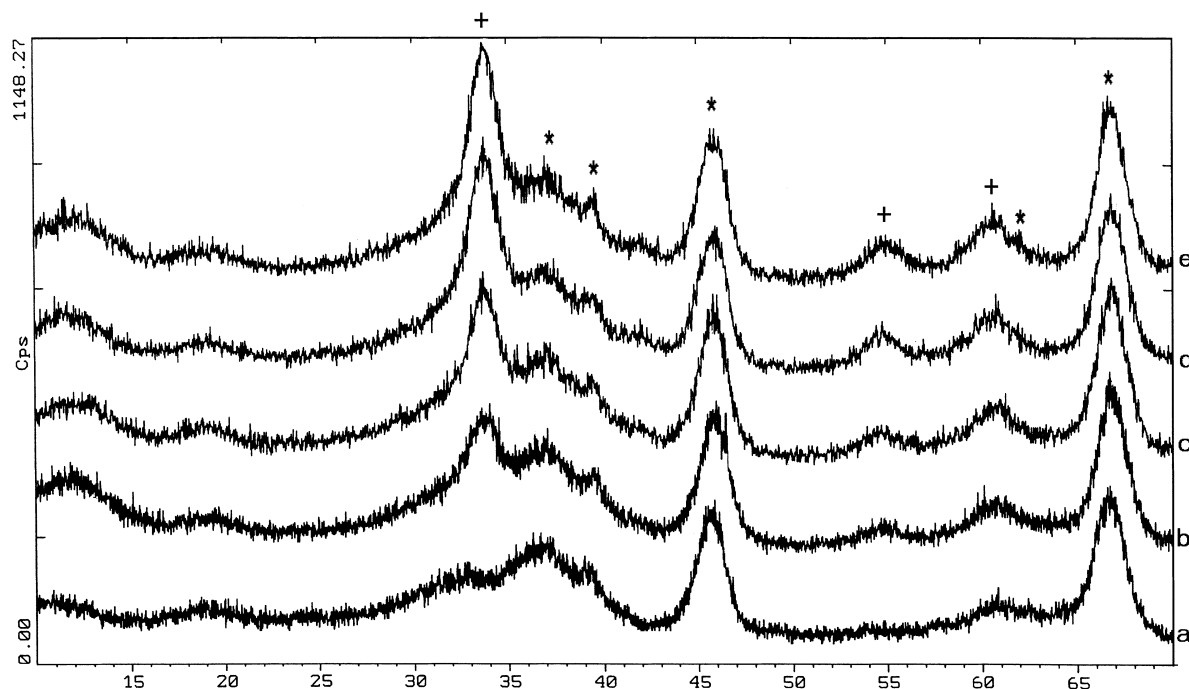


Fig. 4. XRD patterns of Fe-Pd/Al₂O₃ catalysts (unreduced) prepared by conventional heating (CH) (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd. PdO (+); γ -Al₂O₃ (*).

The XRD pattern for metallic Pd has peaks at positions very similar to γ -Al₂O₃ (Pd, 2θ 40.1 and 46.7°; γ -Al₂O₃, 2θ 36.5, 39.5, ca. 46 and 67°). This makes unequivocal identification of metallic Pd in the presence of Al₂O₃ difficult. However, the XRD patterns of both conventionally heated catalysts (LTR, Fig. 7 and HTR, Fig. 8) show some evidence for the formation of metallic Pd in the case of monometallic Pd catalysts (Figs. 7e and 8e). The XRD pattern for the HTR monometallic Fe catalyst (Fig. 8a) also indicates the presence of metallic Fe (2θ 44.7°). However, the Pd-rich bimetallic Fe-Pd catalysts exhibit a peak which corresponds to a Pd-Fe alloy (2θ 41.2 and ca. 48° for an Fe-Pd alloy of 48–60% Pd) (Figs. 7d, 8c and 8d). In these studies, it is difficult to identify an alloy peak at 48° because of strong overlap with peaks due to γ -Al₂O₃ in this region. However, peaks indicative of the Fe-Pd alloy are clearly seen at 2θ ca. 41°. Whilst the broadness and overlapping nature of the peaks precludes any accurate measurement of a shift from the pure Pd peak, it is clear from inspection of the

patterns that there is a shift to higher values of 2θ with increasing Fe content (Fig. 8c and d). The formation of Fe-Pd alloys in bimetallic catalysts is not unprecedented [10,22,32]. Shifting of the β -palladium hydride peak in the TPR patterns to lower temperatures for the high Pd content catalysts (Fig. 1b–d) also gives indirect evidence for alloy formation between Pd and Fe: it has been reported [23] that β -palladium hydride is more stable than the bimetallic hydride β -PdFeH.

Thus, we can summarise the significant differences found between catalysts prepared by the two different methods:

- The absence of α -Fe₂O₃ in the XRD patterns for the CH samples gives evidence that the Fe species have a very small particle size in these catalysts, and thus, are highly dispersed.
- α -Fe₂O₃ is only observed in the XRD of the MW monometallic sample, giving evidence of larger particle size, and therefore, poorer dispersion.
- β -Palladium hydride is observed in the CH samples with high Pd content (TPR).

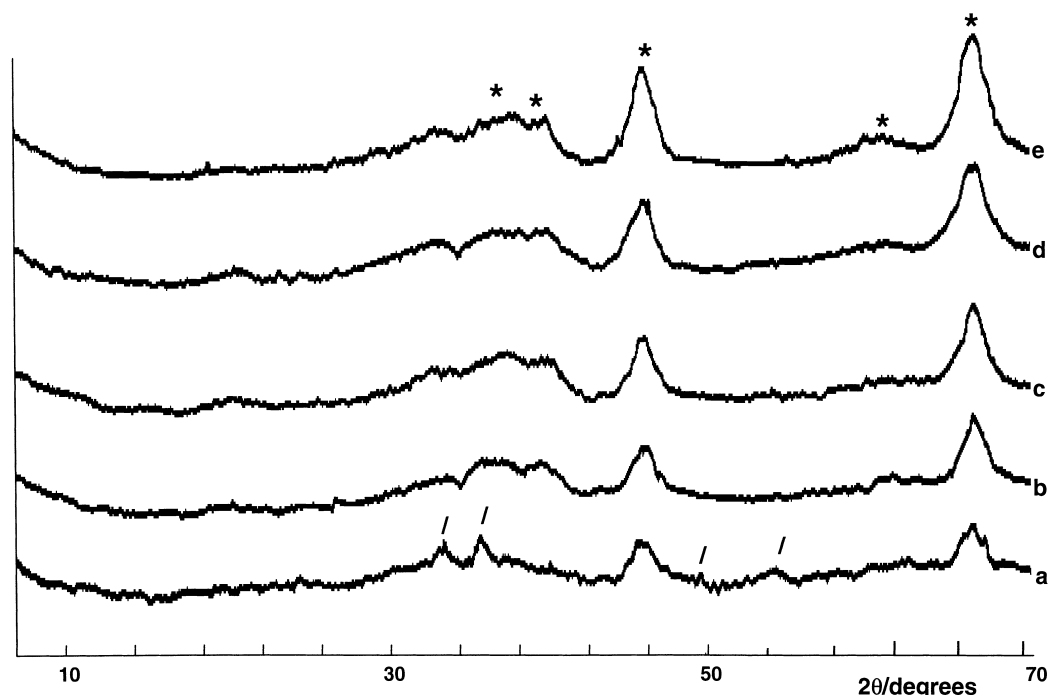


Fig. 5. XRD patterns of Fe–Pd/Al₂O₃ catalysts (LTR) prepared by microwave irradiation: (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd. γ -Al₂O₃ (*); α -Fe₂O₃ (/).

- There is a low temperature reduction peak (ca. 145°C) only in the MW samples (TPR).

It appears therefore that the bimetallic catalysts made by microwave heating are more poorly dispersed, as evidenced by the presence of α -Fe₂O₃ (XRD) and the more clearly defined low temperature reduction peaks in the TPR.

Table 1 gives details of the surface area and hydrogen uptake of the catalysts. The BET surface area of the monometallic microwave catalysts are lower compared to their conventional analogues; however, the hydrogen uptake is greater. This can be explained by the presence of smaller particles of Pd which may block the micropores of the alumina. The interaction of metal with the support depends on the surface density of the hydroxyl groups on the support [24]. Microwaves can interact strongly with hydroxyl groups and this could account for the formation of such particles.

The hydrogen chemisorption data is qualitative [25] since (a) the hydrogen adsorption stoichiom-

etry on bimetallic Pd–Fe catalysts, particularly in the alloyed state, is not clearly identified and (b) hydrogen adsorption on Fe is activated. Hydrogen uptake on the monometallic iron catalyst can be due to adsorption on α -Fe (XRD). Palladium oxide is reduced at temperatures lower than 200°C to palladium metal and this is known [26,27] to increase the hydrogen uptake and facilitate the reduction of iron oxide.

The chemisorption uptake data reveal two significant pieces of information. In the case of the monometallic palladium catalyst, a significant reduction in H₂ chemisorption is observed for the conventionally heated HTR catalyst. Sintering of Pd at high temperature is known to occur during conventional calcination methods of preparation and this is supported by XRD (Fig. 4a). The proposition that microwave heating forms a different kind of Pd species [22] is supported by this observation. In the bimetallic samples, the HTR 50% Pd CH sample showed the greatest evidence of alloy

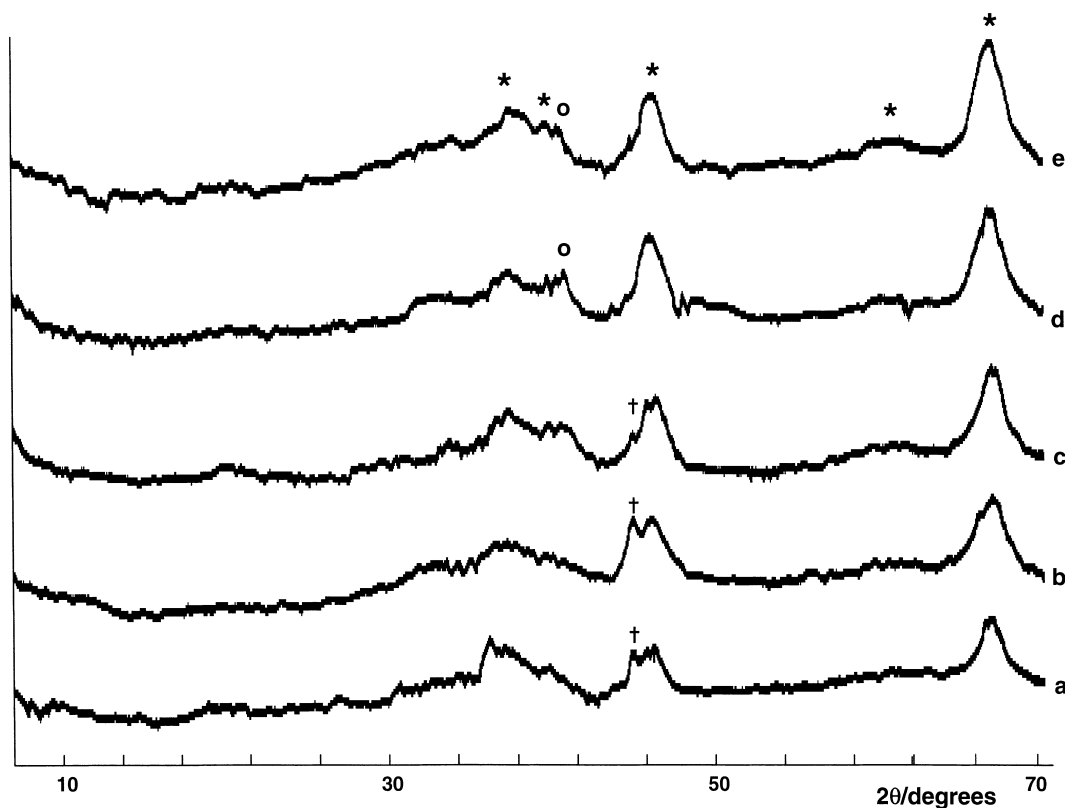


Fig. 6. XRD patterns of Fe–Pd/Al₂O₃ catalysts (HTR) prepared by microwave irradiation: (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd. Fe (+); γ -Al₂O₃ (*).

formation in the XRD. It is in this sample that we see a greatly reduced H₂ chemisorption uptake.

4. Hydrodechlorination activity

Hydrodechlorination of chlorobenzene leads to the formation of three products viz. benzene, cyclohexane and chlorocyclohexane. Under the conditions of the present investigation, the mono- and bimetallic catalysts gave more than 98% selectivity towards benzene. Small amounts of cyclohexane were detected, and there was no formation of chlorocyclohexane. This is consistent with earlier reports [8,9] which showed that, at higher CCl₂F₂ feed composition, addition of a second metal can enhance selectivity, despite reducing the activity because of the dilution effect.

A comparison of the hydrodechlorination activity, in terms of conversion of chlorobenzene to benzene at 140°C following LTR and HTR treatment in conventionally heated and microwave heated catalysts, is given in Figs. 9 and 10, respectively. The patterns recorded at other reaction temperatures (160–200°C) are similar. It is clear that the monometallic Pd catalysts have higher conversions than the bimetallic catalysts *vide supra*. Monometallic Fe catalysts had negligible conversion, and these data are not included. Addition of Fe to Pd has a decreasing effect on conversion. Fig. 10 reveals that a substantial reduction in activity (to below 50%) is observed in the case of conventionally heated bimetallic catalysts subjected to HTR. However, in the case of all microwave-irradiated HTR bimetallic catalysts, this reduction in activity is not nearly so pronounced, and indeed, for one of the catalysts, the conversion approximately doubled to ca. 90%.

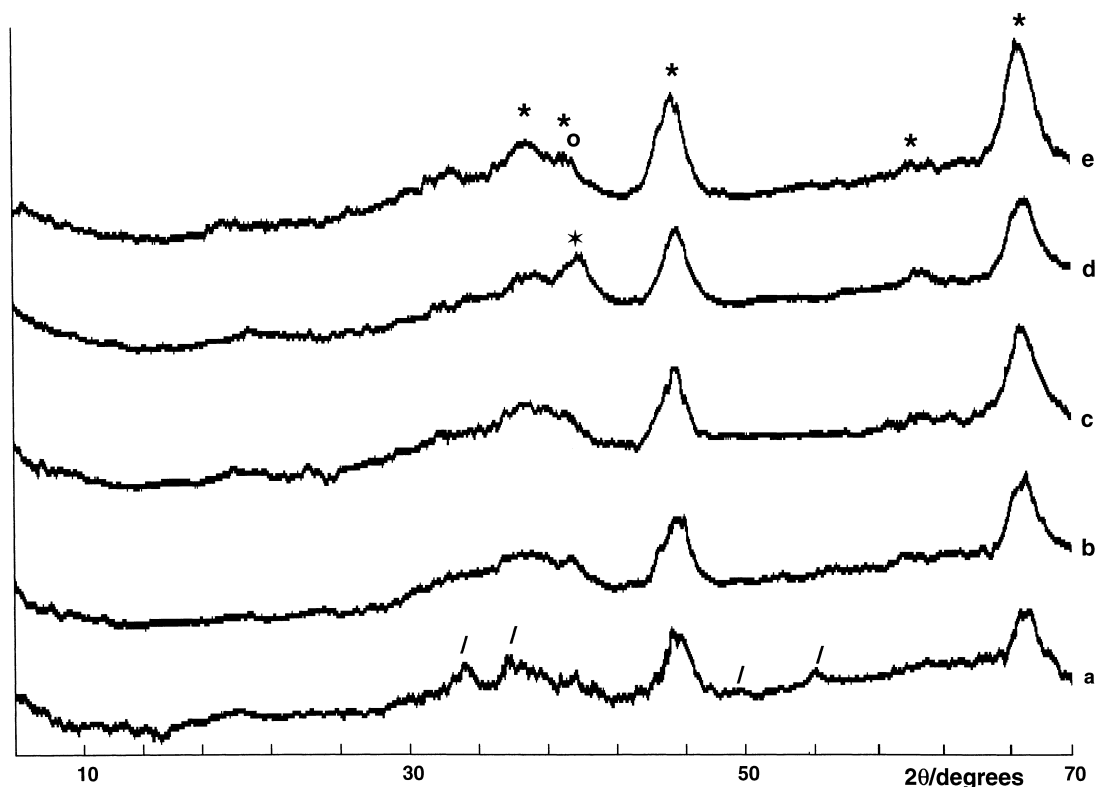


Fig. 7. XRD patterns of Fe–Pd/Al₂O₃ catalysts (LTR) prepared by conventional heating (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd. Pd–Fe alloy (*); Pd (O); γ -Al₂O₃; α -Fe₂O₃ (/).

One of the reasons for the higher activity of MW catalysts after LTR and HTR could be viewed in terms of the particle size effect. Coq et al. [8] in their studies on the hydrodechlorination of chlorobenzene on alumina-supported Pd and Rh catalysts have reported a modest increase in the turn over frequency with increase in particle size. An alternative explanation for the higher activity could be due to the formation of different active species under microwave irradiation (as evidenced by the TPR profiles), for example Pdⁿ⁺ ions, which are reportedly formed and stabilised by the presence of hydroxyl species on alumina surfaces [22]. The catalysts were oven-dried at 120°C before exposure to the microwaves, and hence, are expected to possess substantial moisture content. Microwaves interact strongly with water molecules, and thus, it is possible that microwave heating enhances the transformation of the Pd species by activating the hydroxyl

groups on the surface, and that the Pd species thus formed have better activity for the replacement of Cl by H.

High temperature reduction (HTR) leads to significant changes in the activities (Fig. 10) of both series of catalysts. In the case of HTR bimetallic CH catalysts, there is a substantial reduction in the conversion of chlorobenzene when compared to that of MW catalysts. This is attributed to the formation of a Pd–Fe alloy as evidenced by the XRD patterns [11,28–30]. Even after HTR, the MW catalysts retained their activity, whereas a substantial reduction in activity is shown by the CH catalysts. This is in accordance with the observations that the CH catalysts are more susceptible to alloy formation. The 5% Fe–Pd CH catalyst after HTR showed most evidence of alloy formation (Fig. 8) and also had the lowest H₂ uptake (Table 1). Lowering of activity is clearly due to the formation of Pd–Fe alloy.

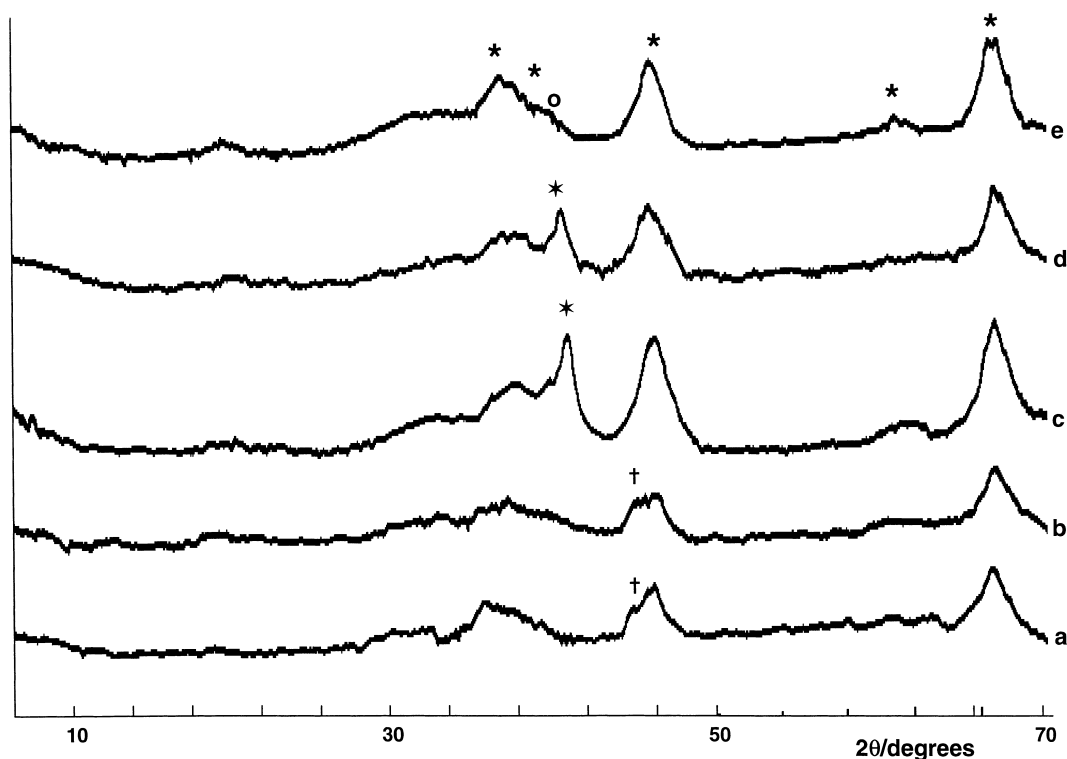


Fig. 8. XRD patterns of Fe–Pd/Al₂O₃ catalysts (HTR) prepared by conventional heating (a) 10% Fe; (b) 7.5% Fe, 2.5% Pd; (c) 5.0% Fe, 5.0% Pd; (d) 2.5% Fe, 7.5% Pd; (e) 10% Pd. Pd–Fe alloy (*); Fe (†); γ -Al₂O₃ (*).

Hydrodechlorination of chlorobenzene on the Pd surface occurs in two stages; chlorination of the Pd and its regeneration by hydrogen. The formation of an alloy affects the rate of hydrogenation of the chlorinated surface. The rate of chlorination, however, is unaffected. Studies on the hydrodechlorination of CCl₂F₂

have shown that Fe–Pd bimetallic catalysts supported on graphite give enhancement of CH₂F₂ selectivity. The formation of CH₄, the total dehalogenated product, is suppressed on Pd–Fe catalysts. Thus, reduction in the hydrodehalogenation activity on Pd in the presence of Fe, during the chlorobenzene hydrodechloro-

Table 1
Surface area and hydrogen uptake data for α -Al₂O₃-supported Pd–Fe catalysts

Catalyst		Conventionally heated catalysts			Microwave irradiated catalysts		
%Pd	%Fe	Surface area (m ² /g)	H ₂ uptake, H/(Pd+Fe), at 25°C (μ mol/g catalyst)		Surface area (m ² /g)	H ₂ uptake, H/(Pd+Fe), at 25°C (μ mol/g catalyst)	
			LTR ^a	HTR ^b		LTR ^a	HTR ^b
0	10.0	184	39.0	42.6	99	46.5	51.1
2.5	7.5	170	52.9	44.6	110	75.6	37.8
5.0	5.0	164	89.2	28.0	167	84.5	50.7
7.5	2.5	151	62.5	70.0	120	52.1	77.9
10.0	0.0	152	112.0	64.1	117	23.0	78.1

^a LTR: low-temperature reduction.

^b HTR: high-temperature reduction.

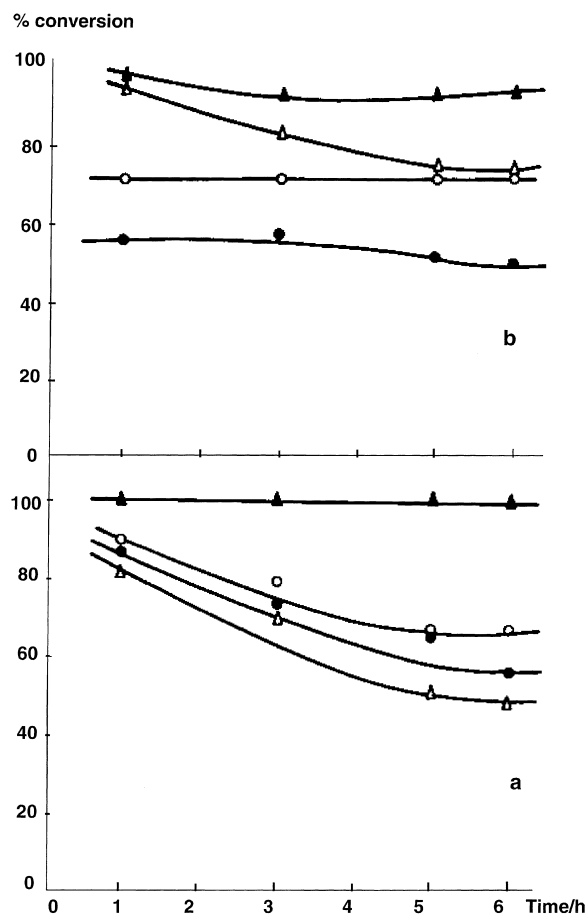


Fig. 9. Time-on-stream analysis of the conversion of chlorobenzene on Fe-Pd/Al₂O₃ catalysts (LTR) prepared by (a) conventional heating; (b) microwave irradiation. 7.5% Fe, 2.5% Pd (○); 5.0% Fe, 5.0% Pd (●); 2.5% Fe, 7.5% Pd (△); 10% Pd (▲).

riation observed in the present investigation agrees with these observations. The alloy phases formed have a reduced hydrogen transfer capability in comparison with a noble metal: the iron atom acts as a barrier to hydrogen migration, thus producing a difference in activity. The XRD patterns of the HTR conventionally heated catalysts show that the formation of α -Fe decreases with increase in Pd content and that eventually alloy formation sets in and α -Fe is no longer observed. The early onset of alloy formation in these samples correlates with the sharp drop in activity as compared with the microwave heated HTR samples.

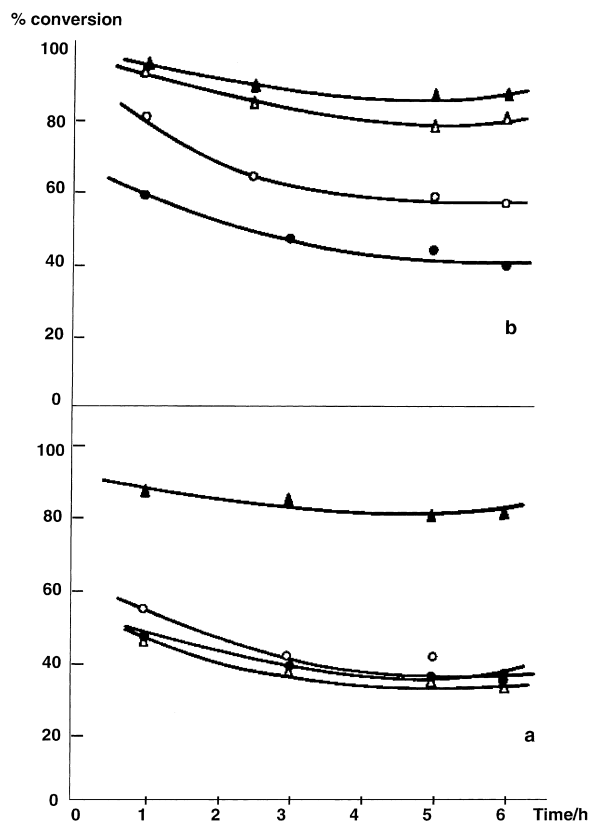


Fig. 10. Time-on-stream analysis of the conversion of chlorobenzene on Fe-Pd/Al₂O₃ catalysts (HTR) prepared by (a) conventional heating; (b) microwave irradiation. 7.5% Fe, 2.5% Pd (○); 5.0% Fe, 5.0% Pd (●); 2.5% Fe, 7.5% Pd (△); 10% Pd (▲).

5. Conclusions

The preparation of Pd-Fe/Al₂O₃ catalysts by microwave irradiation changes the particle size and susceptibility to alloy formation of the catalysts. Comparison of these catalysts with those of the conventionally heated catalysts reveal (i) enhanced crystallite size and (ii) changes in the nature of the palladium species. The Pd species formed during microwave irradiation resist the formation of β -palladium hydride at low temperatures.

Microwave irradiated Pd-Fe catalysts supported on alumina are found to be less susceptible to alloy formation.

Catalysts prepared by microwave irradiation give higher chlorobenzene conversion compared to those

obtained over conventionally heated catalysts under all the experimental conditions used in the present study. Increased particle size, less facile alloy formation and a favourable change in the nature of palladium may account for this behaviour.

Acknowledgements

The authors are indebted to The British Council, UK and CSIR, India for funding the Link programme. Thanks are due to the Director, IICT, Dr. K.V. Raghavan for his encouragement and interest in the project. One of the authors, NL, thanks UGC, New Delhi for the award of a research fellowship.

References

- [1] R. Dagani, Chem. Eng. News 75 (1997) 26.
- [2] A.C. Metaxas, J.G.P. Binner, in: J.G.P. Binner (Ed.), Advanced Ceramic Processing and Technology, Vol. 1, Noyes Publications, 1990.
- [3] P.S. Sai Prasad, N. Lingaiah, P. Kanta Rao, F.J. Berry, L.E. Smart, Catal. Lett. 35 (1995) 345.
- [4] B.F. Hagh, D.T. Allen, Catalytic Hydrodechlorination of Innovative Hazardous Waste Treatment Technology, Vol. 1, Freeman, Technomic, Lancaster, PA, 1990.
- [5] S. Okazaki, A. Kurosaki, Chem. Lett. 11 (1989) 1901.
- [6] B.F. Hagh, D.T. Allen, Chem. Eng. Sci. 45 (1990) 2395.
- [7] P.N. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967.
- [8] B. Coq, S. Hub, F. Figuéras, D. Tournigant, Appl. Catal. A 101 (1993) 41.
- [9] B. Coq, G. Ferrat, F. Figuéras, J. Catal. 101 (1986) 434.
- [10] G. Lietz, M. Nimz, J. Völter, K. Lázár, L. Guzzi, Appl. Catal. 45 (1988) 71.
- [11] P. Bodnariuk, B. Coq, G. Ferrat, F. Figuéras, J. Catal. 116 (1989) 459.
- [12] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, J.A. Moulijn, Appl. Catal. A 155 (1997) 59.
- [13] S. Deshmukh, J.L. d'Itri, Catal. Today 40 (1998) 377.
- [14] W. Juszczuk, A. Malinowski, Z. Karpinski, Appl. Catal. A 166 (1998) 311.
- [15] A. Malinowski, W. Juszczuk, M. Bonarowska, J. Pielaszek, Z. Karpinski, J. Catal. 177 (1998) 153.
- [16] J.E. Benson, H.S. Hwang, M. Boudart, J. Catal. 30 (1973) 146.
- [17] A.L. Bonivardi, M.A. Baltanas, J. Catal. 138 (1992) 500.
- [18] E.E. Unmuth, L.H. Schwartz, J.B. Butt, J. Catal. 87 (1983) 8.
- [19] H.F.J. van't Blik, J.W. Niemantsverdriet, Appl. Catal. 10 (1984) 155.
- [20] F.J. Berry, L. Liwu, W. Chengyu, T. Renyuan, Z. Su, L. Dongbai, J. Chem. Soc., Faraday Trans. 1 81 (1985) 2293.
- [21] F.J. Berry, S. Jobson, Xu Chenghai, J. Chem. Soc., Faraday Trans. 86 (1990) 165.
- [22] R. Wunder, J. Phillips, J. Phys. Chem. 98 (1994) 12329.
- [23] F.A. Lewis, Platinum Met. Rev. 26 (1982) 121.
- [24] W. Juszczuk, Z. Karpinski, I. Ratajczykowa, Z. Stanasiuk, J. Zielinski, L.L. Sheu, W.M.H. Sachtler, J. Catal. 120 (1989) 68.
- [25] S.T. Homeyer, L.L. Sheu, Z. Zhang, W.M.H. Sachtler, V.R. Balse, J.A. Dumesic, Appl. Catal. 64 (1990) 225.
- [26] A. Sárkány, Z. Zsoldos, B. Furlong, J.W. Hightower, L. Guzzi, J. Catal. 141 (1993) 566.
- [27] L. Xu, G-D. Lei, W.M.H. Sachtler, R.D. Cortright, J.A. Dumesic, J. Phys. Chem. 97 (1993) 11517.
- [28] R.L. Garten, D.F. Ollis, J. Catal. 35 (1974) 232.
- [29] M. Boudart, in: G.C. Bond, P.B. Wells, F.C. Tompkins (Eds.), in: Proceedings of 6th International Congress on Catal., London, 1976, Vol. 1, Chemical Society, London, 1976, p. 1.
- [30] A.G. Ruiz, A.S. Escibano, I.R. Ramos, Appl. Catal. A 81 (1992) 101.
- [31] G. Bond, R.B. Moyes, D.A. Whan, Catal. Today 17 (1993) 427.
- [32] H. Lieske, G. Lietz, W. Hanke, J. Völter, Z. Anorg. Allg. Chem. 527 (1985) 135.