Studies on magnesia supported mono- and bimetallic Pd-Fe catalysts prepared by microwave irradiation method

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Abstract

Magnesia supported mono- and bimetallic Pd-Fe catalysts were prepared by conventional and microwave irradiation method. The prepared catalysts were characterised by N_2 adsorption, temperature programmed reduction, selective hydrogen chemisorption and X-ray diffraction (XRD). The conventionally prepared catalysts after high temperature reduction (HTR) showed the formation of Pd-Fe alloy. In the case of microwave irradiated catalysts the formation of Pd-Fe alloy is limited during HTR reduction. These catalysts activity was tested in hydrodechlorination (HDC) of chlorobenzene. The catalysts prepared by microwave irradiation method are more active compared to conventionally prepared ones. The microwave irradiation leads to different morphology of the bimetallic catalysts. The HDC activity results are discussed in terms of structural differences between the catalysts prepared by conventional and microwave irradiation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Bimetallic catalysts have been used in industrial process for many years because of their unique catalytic properties. However, it has only been comparatively recently that an understanding of the structure changes as a function of preparation method and treatment has been developed [1,2]. It is also clear that most structural studies have focused on noble metal/base metal system [3]. Yet, of equal industrial importance are noble metal/noble metal catalysts [4]. There is reason to believe that the structural behaviour of particles containing two noble metals will be significantly different than those containing a noble metal and a base metal. Most of the work published on bimetallic catalysts was in the selective hydrogenation reactions. On the other hand recently lot of research has been focused on the catalytic hydrodechlorination (HDC). The catalytic HDC is an important process for wastewater treatment, disposal or recycling of chlorinated hydrocarbons and in the manufacture of fine chemicals [5,6]. This HDC is similar to that of hydrogenation reaction and the hydrogenation catalysts are also found to be active for this reaction. For this reaction Pd based catalysts are found to be effective. The addition of second metal such as Fe, Co or K to Pd can influence the selectivity and stability in the HDC reaction [7]. The HDC activity is found to be effected by Pd particle size, nature of support and the morphology of bimetal, which in turn depends on the method of preparation [8]. Recently the preparation of

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catalysts by microwave irradiation has been developing as an effective technique. The main advantages of this technique in the preparation of catalysts are rapid drying and uniform distribution of active compound due to moisture levelling and physically strong pellet [9]. The catalysts prepared by this method have a different morphology when compared with conventionally prepared catalysts. In our earlier study over the Pd supported on alumina and silica catalysts prepared by both conventional and microwave irradiation method in benzene hydrogenation found that the catalysts prepared by later method were more active [10]. There are not many published works over the bimetallic catalysts prepared by microwave irradiation. Most of the work reported on this reaction deals with the metal(s) supported on commonly used supports like alumina, silica and carbon. Magnesia is an interesting catalyst support due to its ability to stabilise the metal in unusual oxidation states and to prevent sintering and volatilisation. Ion migration is also expected to be more on magnesia and microwave irradiation might lead different morphology on magnesia compared to other supports. The present investigation focused on the changes in the morphology of bimetallics during the microwave irradiation and their effect in the catalytic activity.

In this study mono- and bimetallic Pd and Fe supported on magnesia catalysts were prepared by conventional and microwave irradiation and their activity were tested in the HDC of chlorobenzene.

2. Experimental

The support, magnesia was prepared by the calcination of magnesium carbonate (LOBA Chemie, AR Grade) in air at 600°C for 6 h. The Pd-Fe supported on magnesia catalysts were prepared by impregnation method using required amounts of aqueous iron nitrate and palladium nitrate solutions by fixing constant loading of 10 wt.% of active component. After allowing the adsorption for overnight, the excess solution was evaporated on a water bath and the partially dried material was then heated in air oven at 120°C for 12 h. Then the catalyst materials were divided into two parts. The first part of each catalyst was calcined in air at 450°C for 5 h to prepare the catalyst by conventional method. The second portion of dried catalyst was subjected to microwave heating

at 100% power for a period of 5 min in a microwave oven (CEM Corporation, USA). Thus, prepared catalysts are termed as catalysts prepared by microwave irradiation.

X-ray diffraction (XRD) patterns of the fresh and reduced samples were recorded on a Siemens D-5000 or a Phillips PW 1051 diffractometer using Cu Kα radiation. BET surface area was determined by nitrogen adsorption at −196°C using an all glass high vacuum apparatus. The same apparatus was used to determine hydrogen uptake capacities at room temperature of the catalysts reduced in hydrogen flow at 250°C, low temperature reduction (LTR) or at 525°C, high temperature reduction (HTR). The double isotherm method was used for this purpose. Temperature programmed reduction 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 in a fixed bed microreactor system at atmospheric pressure in the temperature range 140–200°C. Before starting the reaction the catalysts prereduced in a flow of pure hydrogen (60 ml/min, 2 h) at 250 or 525°C, as the case may be. After bringing the reaction temperature to the required level, chlorobenzene was fed by means of a microfeed pump into the reactor in which the catalyst was suspended between two quartz plugs. Purified hydrogen at a molar ratio of chlorobenzene:hydrogen equal to 1:3 was also admitted into the preheater zone of the reactor. The time on stream analysis carried out on these catalysts revealed that after 6 h, the decrease in conversion was negligible. The products were condensed in a cold trap after attaining steady state conditions (6 h) and analysed by gas chromatography using FID detector and a carbowax-20 M column.

3. Results and discussion

Table 1 shows the physical characteristics of Pd-Fe/MgO catalysts prepared by conventional and microwave irradiation methods. Microwave irradiation resulted in reduction of surface area compared to conventionally heated catalysts. Microwave heating might be leading to enhance the particle size of the active component.

Table 1
Physical characteristics of magnesia supported mono- and bimetallic Pd-Fe catalysts

Catalyst	Pd (%)	Fe (%)	Pd/Fe atomic ratio	Surface area (m^2/g) of conventionally heated catalysts	Surface area (m^2/g) of microwave irradiated catalysts
FPM-1	0	10	–	15	8
FPM-2	2.5	7.5	0.18	19.6	8.5
FPM-3	5	5	0.53	21	10
FPM-4	7.5	2.5	1.59	21.8	9
FPM-5	10	0	–	19	7

3.1. Temperature programmed reduction

The reduction profiles of the conventionally heated catalysts are presented in Fig. 1. The mono-metallic Pd catalyst (Fig. 1e) shows two distinct peaks centered at 156 and 360°C. The peak at lower temperature (156°C) was due to the reduction of PdO. Generally, the reduction of PdO shows a single reduction peak at low temperature. However, in the present study on magnesia support it observed two reduction peaks. The HTR peak might be due to the reduction of Pd interacted with magnesia. Magnesia was known to be an interacting support. The pattern of the mono-metallic iron catalyst (Fig. 1a) also show two broad peaks with maxima at 430 and 570°C, revealing the two-stage reduction of Fe_2O_3 to Fe through Fe_3O_4 [11]. The
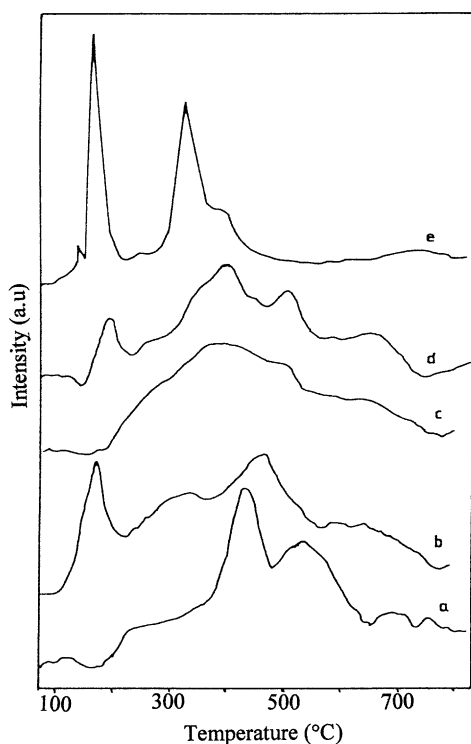

Fig. 1. Temperature programmed reduction profiles of Pd-Fe/MgO catalysts prepared by conventional heating method. (a) 10 wt.% Fe; (b) 7.5 wt.% Fe, 2.5 wt.% Pd; (c) 5 wt.% Fe, 5 wt.% Pd; (d) 2.5 wt.% Fe, 7.5 wt.% Pd; (e) 10 wt.% Pd.
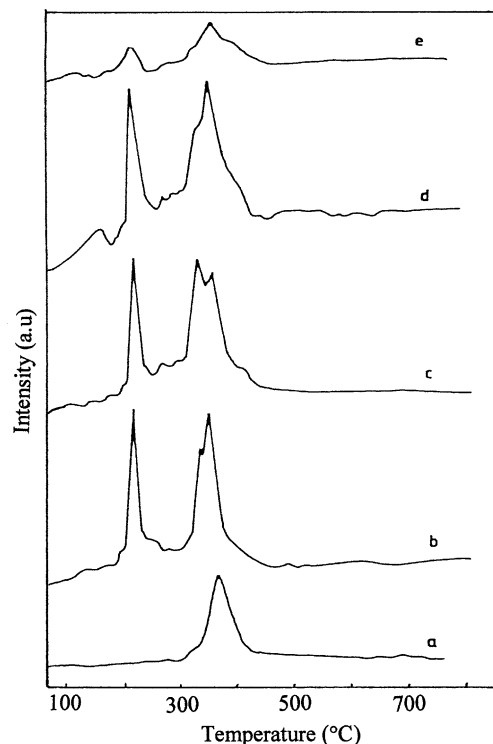

Fig. 2. Temperature programmed reduction profiles of Pd-Fe/MgO catalysts prepared by microwave irradiation method. (a) 10 wt.% Fe; (b) 7.5 wt.% Fe, 2.5 wt.% Pd; (c) 5 wt.% Fe, 5 wt.% Pd; (d) 2.5 wt.% Fe, 7.5 wt.% Pd; (e) 10 wt.% Pd.

HTR in iron oxide catalysts arises as reported earlier due to difficulty in the reduction of well dispersed iron because of inhibition of the nucleation [12]. The bimetallic samples show a decrease in peak maxima when compared to that of mono-metallic ones. It is well-known that the reduction of iron, which generally proceeds at higher temperatures, was enhanced by the presence of noble metal palladium [13]. The maxima of the two peaks corresponding to the first and second stages of reduction have decreased with the addition of Pd to Fe. Absence of the negative peak at higher Pd content and other compositions suggest a strong interaction between Pd and Fe as well as the magnesia support.

TPR profiles of microwave treated catalysts are drawn in Fig. 2. The mono-metallic Pd catalyst shows a similar type of pattern to that of conventional system, excepting lower intensity of peaks. The mono-metallic Fe catalyst was showing a different TPR pattern when compared to conventional system. It is giving a single reduction peak whereas in conventional prepared one it has undergone a two-stage reduction. The single peak at about $400°C$ corresponding to Fe^{3+} reduction to Fe^{2+} and no further reduction of Fe^{2+} to Fe^0. This observation was in accordance with Guczi et al. who has reported formation of high percentage of Fe^{2+} and hindering the formation of α-Fe on the MgO promoted Pd-Fe catalysts [14]. When compared to the conventionally heated catalysts, the microwave irradiated bimetallic catalysts have shown considerable change in their TPR spectra. The high temperature peak corresponding to Fe^{2+} reduction to Fe^0 is conspicuously absents in all the profiles.

3.2. XRD analysis

XRD patterns of the fresh catalysts prepared by conventional heating are presented in Fig. 3. The main peaks are associated with crystallinity of magnesia support. In microwave treated catalysts the XRD patterns (Fig. 4) shows not only the peaks corresponding to magnesia but also some more unidentified peaks. The patterns also show some phase transformation that has occurred during the microwave treatment. Less intense peaks related to $Mg(OH)_2$ are observed. It is known that the periclase–brucite transformation is facile in the presence of water or the hydroxyl groups [15]. The catalysts were dried at $120°C$ before exposure to the microwave irradiation and are expected to possess substantial moisture content. Microwaves strongly interact with dipolar molecules like water and it is possible that the microwave heating enhances the periclase–brucite transformation. Appearance of $Mg(OH)_2$ after the microwave irradiation implies such a transformation is enhanced during the microwave irradiation.

Diffractograms of the conventionally and microwave heated catalysts after LTR are also carried
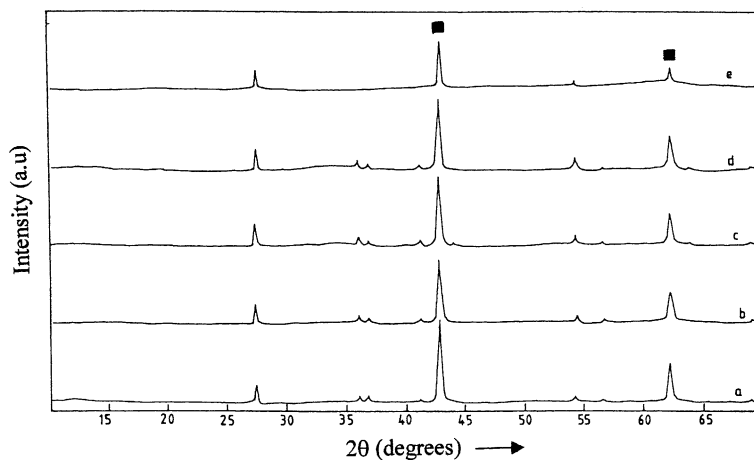

Fig. 3. XRD patterns of Pd-Fe/MgO (fresh) catalysts prepared by conventional heating method. (a) 10 wt.% Fe; (b) 7.5 wt.% Fe, 2.5 wt.% Pd; (c) 5 wt.% Fe, 5 wt.% Pd; (d) 2.5 wt.% Fe, 7.5 wt.% Pd; (e) 10 wt.% Pd ((■), MgO).
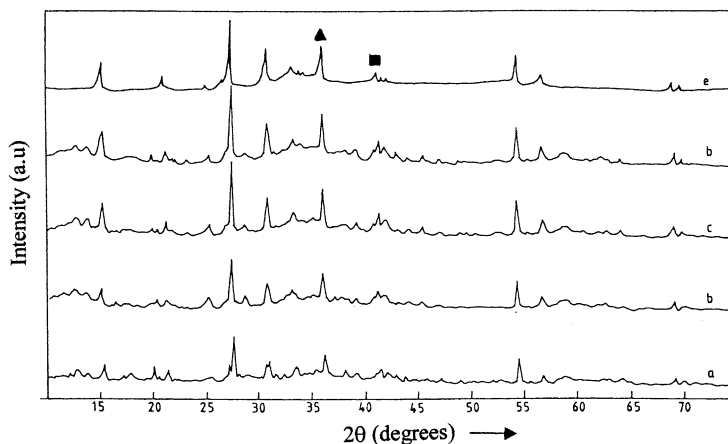
Fig. 4. XRD patterns of Pd-Fe/MgO (fresh) catalysts prepared by microwave irradiation method. (a) 10 wt.% Fe; (b) 7.5 wt.% Fe, 2.5 wt.% Pd; (c) 5 wt.% Fe, 5 wt.% Pd; (d) 2.5 wt.% Fe, 7.5 wt.% Pd; (e) 10 wt.% Pd ((■), MgO; (▲), Mg(OH)₂).

out. However, there observed no significant information from the patterns except MgO–Mg(OH)₂ transformation.

XRD patterns of high temperature reduced conventionally heated catalysts are shown in Fig. 5. The mono-metallic iron catalyst is showing the patterns related to α-Fe. Whereas mono-metallic Pd catalyst reveals the formation of α-Pd. All the bimetallic catalysts show the peaks corresponding to Pd-Fe alloy [16]. However, the intensity of the peaks are low. The intensity of the Pd-Fe alloy peak is increasing with the increase in Pd content. With the increase in the intensity of the alloy peak, as the Pd content increases, there is a simultaneous decrease in α-Fe formation. At higher Pd loading no α-Fe was observed.
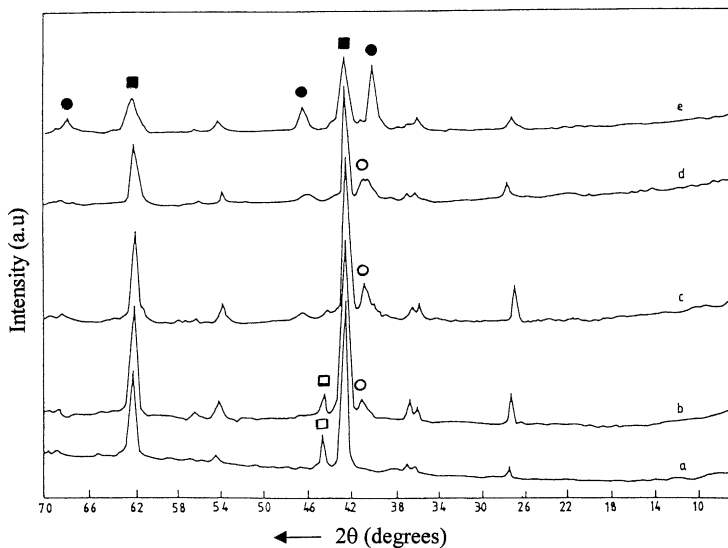

Fig. 5. XRD patterns of Pd-Fe/MgO catalysts prepared by conventional heating method after HTR. (a) 10 wt.% Fe; (b) 7.5 wt.% Fe, 2.5 wt.% Pd; (c) 5 wt.% Fe, 5 wt.% Pd; (d) 2.5 wt.% Fe, 7.5 wt.% Pd; (e) 10 wt.% Pd ((■), MgO; (●), α-Pd; (□), α-Fe; (○), Pd-Fe alloy).
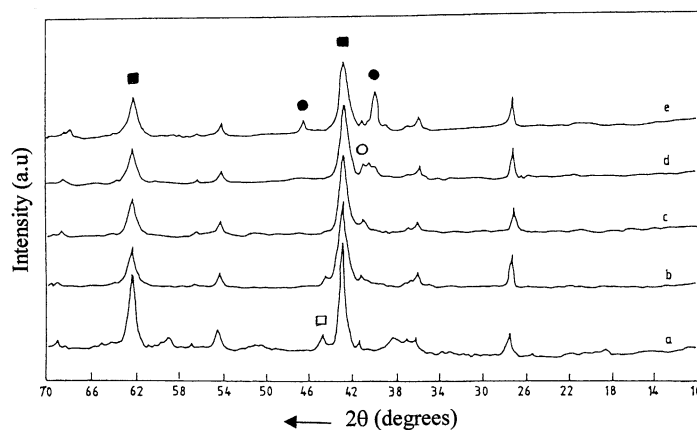
Fig. 6. XRD patterns of Pd-Fe/MgO catalysts prepared by microwave irradiation method after HTR. (a) 10 wt.% Fe; (b) 7.5 wt.% Fe, 2.5 wt.% Pd; (c) 5 wt.% Fe, 5 wt.% Pd; (d) 2.5 wt.% Fe, 7.5 wt.% Pd; (e) 10 wt.% Pd (($\blacksquare$), MgO; ($\bullet$), α-Pd; ($\square$), α-Fe; ($\bigcirc$), Pd-Fe alloy).

Fig. 6 shows the XRD patterns of the microwave irradiation catalysts after HTR. Broadly speaking, the reduction behaviour of these catalysts is almost similar to those of conventionally heated catalysts except the formation of Pd-Fe alloy. In this case the alloy formation is suppressed to a greater extent as peaks are of very low intensity. As in the case of HTR conventionally heated catalysts, these microwave irradiated HTR catalysts also exhibit the majority of the peaks due to MgO.

3.3. Hydrogen chemisorption

The hydrogen chemisorption data obtained on Pd-Fe bimetallic catalysts is quantitative because the hydrogen adsorption stoichiometry on Pd-Fe catalysts is not clearly identified and adsorption of hydrogen on iron is activated. However, the hydrogen chemisorp-

tion data on these catalysts reveals some significant information. The hydrogen chemisorption data on Pd-Fe/MgO catalysts reduced at LTR and HTR are summarised in Table 2.

The hydrogen uptake values of low temperature reduced conventionally heated catalysts show increasing hydrogen uptake as the Pd content increases. It is reported that on magnesia formation of α-Fe is hindered and a high percentage of Fe^{2+} is retained [14] thus, leaving higher number of unalloyed Pd sites exposed for chemisorption. From the chemisorption behaviour of the present catalysts, it appears that Fe^{2+} is more predominant on magnesia supported catalysts. As further reduction of Fe^{2+} to Fe^0 is limited, formation of Pd-Fe alloy is also limited leaving more and more unalloyed Pd sites exposed for hydrogen chemisorption as the Pd content increases. Hence an increase in hydrogen uptake was observed. Though,

Table 2

Hydrogen chemisorption data of magnesia supported mono- and bimetallic Pd-Fe catalysts after LTR and HTR

Catalyst code	Conventianally heated catalysts chemisorption (μmol/g cat)		Microwave irradiated catalysts chemisorption (μmol/g cat)	
	LTR	HTR	LTR	HTR
FPM-1	19.2	38.4	27.2	38.2
FPM-2	24.8	22.1	42.9	40.6
FPM-3	57.9	37.1	55.3	47
FPM-4	66.5	51.7	64.7	59.5
FPM-5	67.4	61.3	73.4	59.1

the XRD patterns of the low temperature reduced conventionally heated catalysts do not reveal a clear indication of the partially reduced phase, possibly due to microcrystallinity, predominance of the first reduction peak ($Fe^{3+} \rightarrow Fe^{2+}$) compared to second ($Fe^{2+} \rightarrow Fe^0$) in the TPR patterns of these catalysts supplement this argument. In the case of low temperature reduced microwave irradiated catalysts also a similar behaviour was observed. The TPR profiles clearly exhibit the stabilisation of Fe^{2+} on MgO. The absence of alloy formation further substantiates this observation. The periclase–brucite transformation showed in microwave treated catalysts that appear to prevent the crystallisation of both Fe and Pd oxides.

HTR has brought the following changes in the adsorption capacities of the two systems of the catalysts. Adsorption capacities have decreased to a considerable extent when compared to LTR treated catalysts. The reason might be the formation of alloy phase in case of these catalysts as observed from XRD. It is reported that the alloy has a lower adsorption capacity. Further, the alloy particles on MgO supported catalysts maintain considerable high dispersion. However, the mono-metallic Fe catalysts recorded an increased hydrogen uptake, which may be due to enhanced reducibility of Fe when subjected to higher temperatures, since reduction of Fe is an activated process. In the case of high temperature reduced microwave irradiated bimetallic catalysts, alloy formation is limited because of the Fe^{2+} stabilisation on MgO as evidenced

by TPR patterns. Decreased adsorption capacities after high temperature treatment in case of magnesia based catalysts could also occur to the decoration of the active species with MgO. Datye and Logan reported that the partial solubility of the acidic oxides, possibly of Fe, in the $Mg(OH)_2$ and its subsequent heating could result into reduced hydrogen uptakes [15].

3.4. HDC of chlorobenzene activity

The HDC of chlorobenzene resulted benzene (>98%) as the only organic product. HDC reaction rates of the conventional heated and microwave irradiated LTR and HTR catalysts at reaction temperature of 140°C are presented in Fig. 7. The mono-metallic Pd catalyst (Fe loading is zero) has shown the highest reaction rate in both the cases. A decrease in the activity was observed with the addition of Fe to Pd. However, the activity remains constant with further addition of Fe. Mono-metallic Fe has no HDC activity at all. The microwave treated catalysts are showing better activity than the corresponding conventionally prepared catalysts.

A sudden decrease in the catalytic activity with the addition of Fe to Pd may be explained as a dilution effect. Addition of less active second metal Fe results into a decrease in the number of surface Pd atoms. Coq et al. explains the activity fall with addition of second metal in terms of lowering the rate of reduction of chlorinated surface which was formed during the
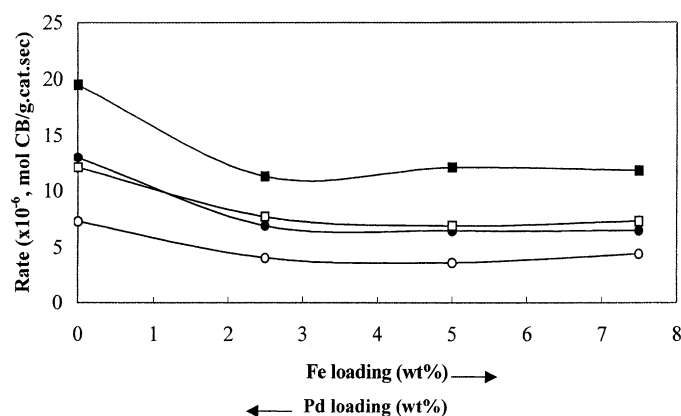

Fig. 7. HDC of chlorobenzene activity patterns of the Pd-Fe/MgO catalysts prepared by conventional (CH) and microwave irradiation (MH) method after LTR and HTR. Reaction temperature: 140°C ((●), CH/LTR; (■), MH/LTR; (○), CH/HTR; (□), MH/HTR).

reaction with HCl produced in the reaction [8]. As the interaction of HCl with the basic sites on MgO is facile. The reduction of Pd-Cl to active Pd-H is difficult if the support contains Cl ions.

The question that arises at this point is how the microwave heated catalysts are showing better activity than conventionally heated catalysts. It is reported that the modest enhancement in the TOF during HDC of CB with increase in particle size [6]. However, no such prominent increase in particle size was observed by XRD and from H_2 uptake data. Juszczyk et al. has suggested that the formation of Pd^{n+} ions is favourable in presence of hydroxyl groups on the surface [17]. As discussed in XRD section, the microwave irradiation might be favouring the periclase–brucite transformation due to the presence of moisture content and leading to sufficient number of $Mg(OH)_2$ species. Since the magnesia surface possesses abundant $Mg(OH)_2$ species after microwave irradiation it is possible that the transformation of Pd species to Pd^{n+} ions is feasible. The existence of $Mg(OH)_2$ after microwave treatment as evidenced by XRD and the absence of negative peak in TPR (e.g. in mono-metallic Pd catalyst) which is correspond to β-PdH decomposition supplements this proposition. It can be envisaged that the Pd^{n+} ion formation is accelerated by the application of microwave irradiation. Hence, it can be proposed that the existence of Pd^{n+} ions stabilised by the magnesia support may be responsible for the enhanced HDC activity.

When the reduction temperature is increased from 250 to 525°C a decrease in specific activity was observed in both conventional and microwave treated catalysts. The HTR might affect the metal particles. A decrease in H_2 chemisorption for HTR catalysts in comparison with LTR suggests the change in the catalyst particles on the surface. A decrease in H_2 uptake

with increase in reduction temperature may be due to reduced H_2 transfer capacity of the alloy phase when compared to the noble metal. An explanation for this inhibited H_2 transfer capacity could be that Fe atoms located at the surface act as a barrier for H_2 migration, thus, limiting the hydrogen transfer process. Formation of Pd-Fe alloy after the HTR was observed from the XRD of conventionally heated catalysts. Alloying Pd with Fe induces a decrease of activity.

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