Microwave irradiation: an effective method for the preparation of low dispersed Pd/Al_2O_3 catalysts used in the hydrodechlorination of CCl_2F_2 to CH_2F_2

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Received 15 November 1999; accepted 13 April 2000

Microwave irradiation is found to be a faster method for the preparation of low dispersed Pd/Al_2O_3 catalysts with higher activity and selectivity to CH_2F_2 in the hydrodechlorination of CCl_2F_2.

Keywords: alumina-supported palladium catalyst, microwave heating, powder X-ray diffraction, temperature-programmed reduction, hydrodechlorination, nitrogen adsorption, hydrogen chemisorption

1. Introduction

Catalytic hydrodechlorination has been identified as a viable alternative for the safe transformation of chlorofluorocarbons (CFCs) which are responsible for depletion of the ozone layer [1,2]. Using Pd-based catalysts, hydrodechlorination has been used to convert CFCs into value-added products. An example [3] is the conversion of CCl_2F_2 (CFC-12) into an environmentally safe product, CH_2F_2, known as HFC-32. Most studies have focused on the role of the support [3–5], the influence of a second metal as promoter [5–8] and the reaction kinetics [4,5,9]. It has been reported [4,10] that for hydrodechlorination reactions, the catalytic activity and the selectivity towards HFC-32 strongly depend on metal dispersion in the $Pd/\gamma\text{-}Al_2O_3$ catalysts; the poorly dispersed Pd catalysts exhibiting higher turnover frequencies. Attempts have been made to increase the Pd particle size by high-temperature reduction [11]; this has little effect on the activity, but leads to increased selectivity towards $C_2H_2F_2$.

Microwave irradiation has been shown to be a promising technique for catalyst preparation [12]. For example [13], during catalyst preparation microwave irradiation leads to moisture levelling, a uniform distribution of active species on the support and physically stronger pellets. In previous work [14], we observed that microwave irradiation increased the particle size of Pd, giving catalysts with high turnover frequency for the hydrogenation of benzene. Application of microwaves in catalyst development has two main effects: (i) changes in the morphology of the catalyst as a result of irradiation during catalyst preparation (such as particle size effects and crystallinity), and (ii) changes in the activity and selectivity during reaction, e.g., super heating, when compared to conventional heating. The objective of this work was to use microwave irradiation as an easy and fast method for the preparation of low dispersed Pd catalysts and to compare their performance with catalysts prepared by conventional methods. We therefore report here on the use of microwave irradiation results in the preparation of Pd/Al_2O_3 catalysts with a lower palladium dispersion, and we also show that these catalysts give a two-fold increase in catalytic activity towards the hydrodechlorination of CCl_2F_2.

2. Experimental

Commercial $\gamma\text{-}Al_2O_3$ (Harshaw 3996-R, crushed to 18/25 BSS mesh, SA = 178 m^2/g) was used as a support. 10 wt% Pd was prepared by impregnating the support with an aqueous solution of palladium nitrate. The suspension was evaporated to near dryness on a water bath and dried in air at 120 °C for 12 h. A portion of the catalyst was subsequently calcined in air at 450 °C for 5 h (CH catalyst) and the remaining portion irradiated in a microwave oven (CEM Corporation, USA) at 100% power (650 W, 2.45 GHz) for 5 min in air (MW catalyst). 5 min was chosen as the irradiation time, as in all cases the maximum temperature (160 °C) in the oven was reached within this period.

Powder X-ray diffraction (XRD) patterns of the conventionally heated (CH) and the microwave heated (MW) catalysts were recorded with a Siemens D-5000 X-ray diffractometer using Cu K_α radiation.

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BET surface areas were determined by nitrogen adsorption at −196 °C using an all-glass high-vacuum apparatus. The same apparatus was used for the determination of room temperature (25 °C) hydrogen chemisorption capacities of the catalysts reduced at 250 °C for 4 h, using a double-isotherm method [15] and revised to eliminate the interference of palladium hydride formation [16].

Temperature-programmed reduction (TPR) of the catalysts were performed using a 10% H_2–90% N_2 gas mixture at a heating rate of 16 °C/min with a gas flow rate of 20 ml/min.

Hydrodechlorination of CCl_2F_2 was carried out in a microreactor interfaced on-line with a gas chromatograph. CCl_2F_2 and hydrogen were mixed in a molar ratio of 1 : 8 and passed over the catalyst bed (approximately 1.0 g) at a space velocity of 4800 h^{-1}. The reaction was carried at reaction temperatures ranging between 160 and 240 °C, after reducing the catalyst in H_2 at 250 °C for 4 h. The time on stream analyses carried out for 20 h did not show any deactivation of the catalysts. Since the difference in activity was negligible after 6 h on stream, the data obtained after 6 h were taken as the steady-state values. The product was scrubbed with KOH to neutralize HCl/HF produced in the reaction and the gas phase product was analyzed in a gas chromatograph using a FID detector and a Porapak-Q column.

3. Results and discussion

The catalyst characterisation data [14], BET surface area, hydrogen uptake, the extent of palladium dispersion and the particle size calculated from hydrogen uptake, are reproduced in table 1. The smaller surface area of the MW catalyst compared to the CH catalyst can be associated with an increase in particle size in the former. Hydrogen chemisorption reveals a considerable difference in the particle sizes of MW and CH (229 vs. 47 Å) catalysts indicating significant weakening in the interaction of the Al_2O_3 support with the palladium precursor during microwave irradiation. The alumina support, previously calcined at 450 °C, does not significantly increase in temperature on microwave irradiation in air for 5 min; the microwaves therefore appear to interact predominantly with the adsorbed palladium species on the surface of the alumina. The XRD patterns of the two catalysts [14] are given in figure 1 and show broad peaks indicating that the Al_2O_3 support is poorly crystalline. XRD lines characteristic of palladium(II) oxide can be seen in the case of the CH catalyst, whereas the same phase is less well characterized in the MW catalyst. Lines due to Pd^0 were not observed in the XRD of the reduced catalysts. It appears that microwave irradiation does not completely overcome the strong interaction of Pd with Al_2O_3. The TPR profiles of the two catalysts [14] are shown in figure 2. The CH catalyst shows a desorption peak at 144 °C corresponding to the decomposition of β-palladium hydride [14,17]; this peak is absent in the profile recorded for the MW catalyst and an absorption peak is seen at 156 °C. This indicates that the Pd species formed during microwave heating is different in character from that formed on the CH catalyst. The nature of this species will be the subject of further investigation. From these studies we conclude that the effect of microwave irradiation results in a lower dispersion of a poorly crystalline palladium-containing species.

A comparison of the activity data, over the first 6 h of reaction, obtained for the CH and MW catalysts is shown

Table 1
Properties of the catalysts.

Catalyst[a]	Surface area (m^2/g)	H_2 uptake (μmol/g-cat.)	Dispersion (%)	Particle size[b] (Å)	Turnover number × 10^3 (molecules/site s)		
					200 °C	240 °C	280 °C
Pd/Al_2O_3 (CH)	152	112	23.8	47	7.1	12.8	16.2
Pd/Al_2O_3 (MW)	117	23	5.0	229	88	111.6	108.3

[a] CH – conventional heating, MW – microwave heating.
[b] Particle size is calculated according to [16].

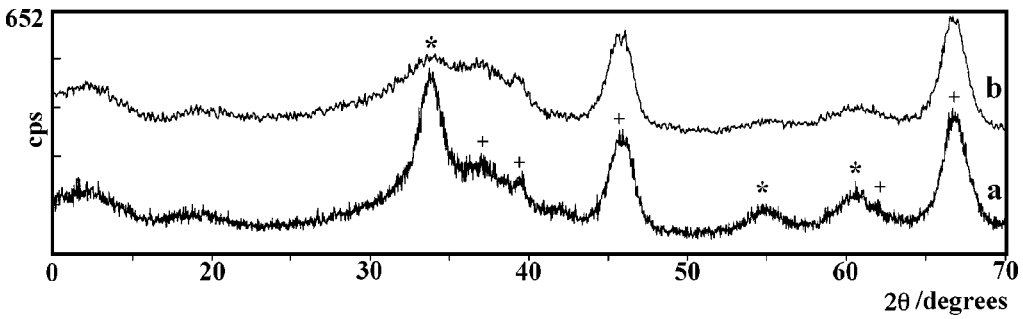

Figure 1. XRD patterns of palladium–alumina catalysts: (a) conventionally heated Pd/Al_2O_3 catalyst and (b) microwave heated Pd/Al_2O_3 catalyst; (∗) PdO + Al_2O_3.

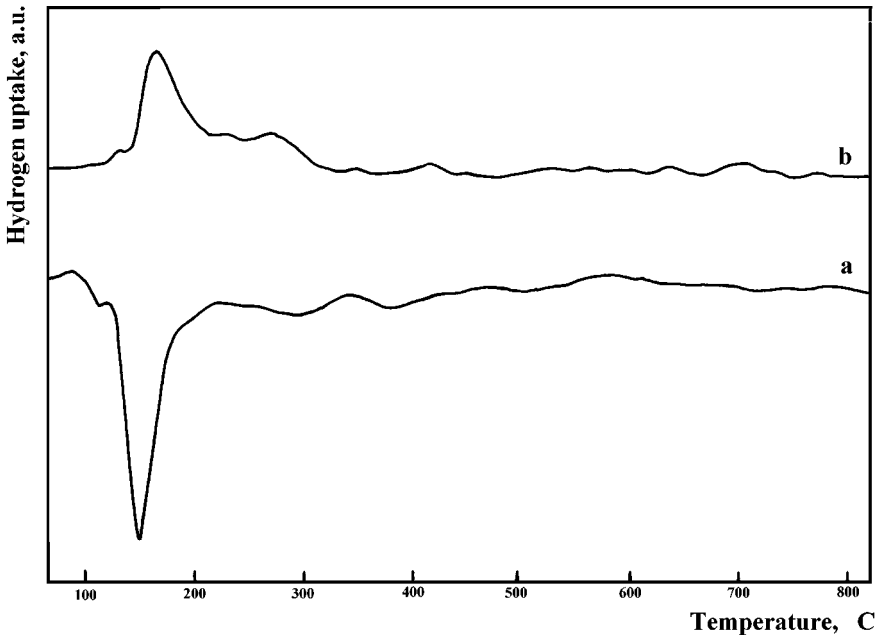

Figure 2. The TPR profiles of Pd/Al_2O_3 catalysts prepared by (a) conventional heating and (b) microwave heating.

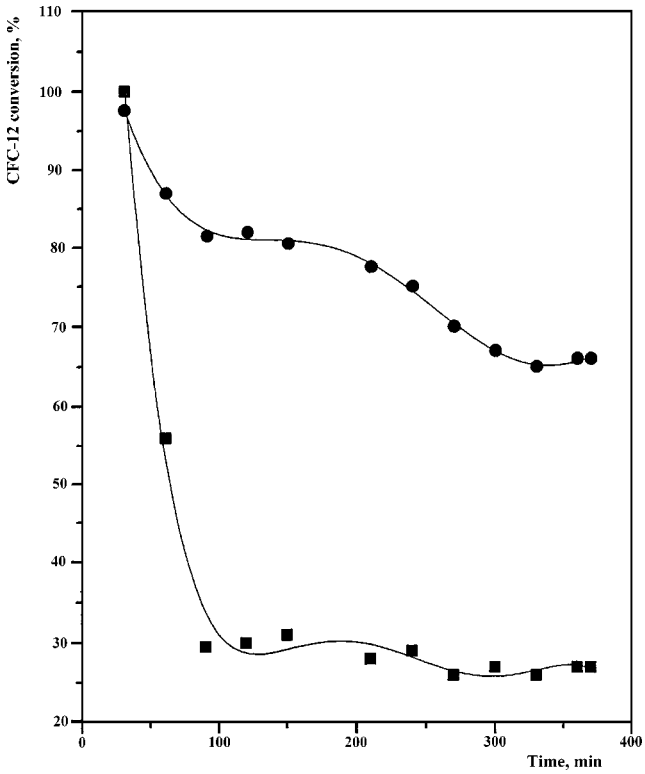

Figure 3. Time on stream analysis of the conversion of CCl_2F_2 to CH_2F_2 on Pd/Al_2O_3 catalysts at a reaction temperature of 200 °C. Catalyst prepared by conventional heating (■) and microwave irradiation (●).

in figure 3. The MW catalyst appears to obtain the steady state at a higher conversion value, whereas the CH catalyst suffers greater loss in initial activity. The steady-state conversion of CCl_2F_2 over the MW catalyst is close to twice that obtained over the CH catalyst. It is known that the Pd catalyst often undergoes reduction in initial activity due to the strong adsorption of HCl liberated as a by-product. However, the higher conversion values in the case of the MW catalyst implies less interaction of HCl with the catalyst, thus increasing the conversion.

Figure 4 compares CCl_2F_2 hydrodechlorination activity and the corresponding yield (the product of conversion and selectivity, divided by 100) towards CH_2F_2 obtained on the MW and CH catalysts in the temperature range 200–280 °C. The activity and yield are consistently higher in the case of the MW catalyst as compared to the CH catalyst. Turnover frequency values for both CH and MW catalysts are given in table 1. The values obtained on CH catalysts are of the same order of magnitude as those reported by Juszczyk et al. [11]. The hydrodechlorination of CCl_2F_2 over palladium catalysts at high reaction temperatures also leads to the formation of partially dehalogenated products such as $CHClF_2$ and the total dehalogenated product, CH_4, which decreases the yield of CH_2F_2.

The hydrodechlorination of CCl_2F_2 on Pd/Al_2O_3 catalysts is currently not well understood. It is thought that initially, Al_2O_3 is converted to $AlO_{1-x}(OF)_x/AlF_x$ during reaction with the HF by-product [18]. During this transformation or passivation stage, Pd/Al_2O_3 exhibits lower selectivity to CH_2F_2. It has been proposed [4] that the subsequent higher selectivity towards CH_2F_2 is associated with this partial formation of AlF_x which withdraws the fluorine atoms, generating electron-deficient Pd species at the metal–support interface, and protecting the Pd particles against diffusion into the bulk. These electron-deficient Pd sites are thought to bind the $CF_2^{\bullet}$ radicals less strongly to favour CH_2F_2 formation [19]. Higher activity has been observed previously on low dispersion catalysts prepared from palladium nitrate [10] and it has been proposed that the formation of palladium carbide could be partially responsible for higher activity as the larger particles are more easily

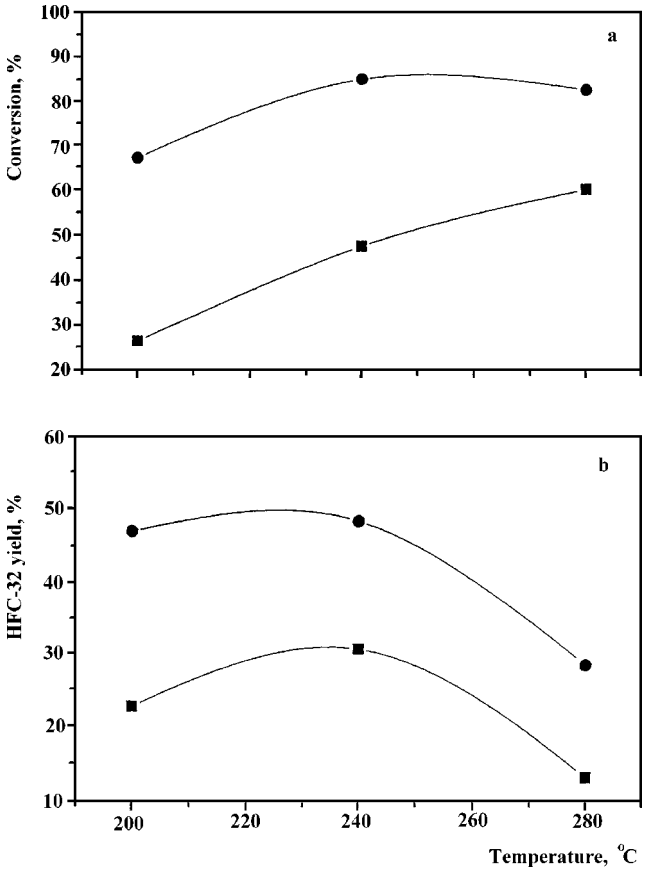

Figure 4. (a) Hydrodechlorination activity and (b) yield of CH_2F_2 as functions of temperature: (■) conventional heating; (●) microwave irradiation. Yield = (conversion × selectivity)/100.

converted into palladium carbide [10,19]. Our results confirm that particle size, dispersion and the nature of the Pd species formed in the preparative process are extremely important.

In summary, microwave irradiation provides an easy and fast method for the preparation of Pd/Al_2O_3 catalysts using palladium nitrate. These catalysts have lower Pd dispersions than conventionally prepared catalysts, and give significantly higher activity and yield in the hydrodechlorination of CCl_2F_2 to CH_2F_2.

Acknowledgement

The authors are indebted to The British Council, UK, and the CSIR, New Delhi, for financial support. Financial support provided by DST, New Delhi, is also acknowledged.

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