Hydrodechlorination of chlorobenzene on Nb$_2$O$_5$-supported Pd catalysts Influence of microwave irradiation during preparation on the stability of the catalyst

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Abstract

Catalytic hydrodechlorination of chlorobenzene was studied on Pd/Nb$_2$O$_5$ catalysts prepared by the conventional and the microwave heating techniques. The catalysts were characterized by X-ray diffraction (XRD), BET surface area, hydrogen chemisorption and scanning electron microscopy (SEM). The time-on-stream studies reveal that the microwave-irradiated catalyst exhibits better resistance towards deactivation than the conventionally prepared catalyst. Microwave irradiation also seems to be preferable than the high-temperature reduction adopted to increase the particle size. The microwave-irradiated catalyst also shows higher residual activity than the electrically heated catalyst at all reaction temperatures studied. This is attributed to the formation of larger particles of palladium which is in conformity with the basic observation made in the literature that hydrodechlorination is more facile on low-dispersed Pd catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodechlorination; Palladium catalyst; Microwave irradiation

1. Introduction

Apart from their mutagenic and carcinogenic activity, the chlorinated hydrocarbons are also recognized as the main culprits for the ozone depletion in the atmospheric stratosphere [1,2]. Hence their production is restricted and efforts are made to collect the existing stocks and dispose them off after converting them into safer compounds, usually by techniques like degradation and incineration. However, these processes are highly energy intensive and liberate toxic chemicals like the dioxines [3].

Catalytic hydrodechlorination has been recognized as a viable technique for the transformation of these compounds into safer and value-added products. Noble metals like Pt [4,5] and Pd [6,7] and non-noble metal like Ni [8] have been extensively used as catalysts for this transformation. Most of the studies, based on Pd catalysts, have been focused on the role of the support [9–11], the influence of a second metal as promoter [12–14] and the reaction kinetics [10,11,15]. It has been reported [10,16] that for

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hydrodechlorination reaction, the catalytic activity and the selectivity towards the required product strongly depend on the particle size of the metal.

During the hydrodechlorination, the HCl produced as a byproduct inhibits the rate of reaction. This deactivation is thought to be due to strong adsorption of the halide species and a consequent blocking of the active sites. The catalyst exhibits an unsteady state with considerable loss in initial activity before a steady residual conversion is achieved. The development of poison-resistant catalyst systems has received utmost importance. In this context, low-dispersed Pd catalysts have been found to possess better resistance towards deactivation. High-temperature reduction, adopted to obtain larger Pd particles, reported during the hydrodechlorination of CCl_2F_2 [16] has shown marginal increase in activity/selectivity. Hence, efforts are on to identify new supports and novel methods of catalyst preparation.

Microwave irradiation is emerging as an important alternative to the conventional electric heating. Several chemical and catalytic syntheses as well as the development of new materials with improved microstructure have been reported using microwave irradiation [17]. Microwave irradiation is reverse to that of conventional heating in terms of thermal gradients and the flow of heat. Whereas conventional heating of a material is by external conduction or convection, microwave heating is generated internally within the material. Both small and larger particles are heated rapidly and uniformly resulting in minimization of thermal stresses, which in turn prevent cracks and enhance microstructure. As an important tool in chemical synthesis, several advantages have been derived by microwave irradiation in terms of shorter process times, improved conversion, enhanced yields, reduction in synthesis temperatures and above all leading to clean solvent-free processes. Application of this dielectric heating is relatively new to catalyst designers. However, its potential has already been reaped [18] in terms of obtaining rapid drying, uniform distribution of active component, physically stronger pellet during preparation of catalysts and increase in conversion, selectivity and significant energy saving during performance. Microwave heating also has the unique feature of providing environmentally friendly processes. Thus, there is a growing interest in its application in process industry.

In this investigation niobium pentoxide, a novel support, has been employed to prepare the Pd catalysts. By means of microwave irradiation during catalyst preparation, an attempt has been made to change the morphology of palladium and to study its effect on the stability of the catalyst towards deactivation taking hydrodechlorination of chlorobenzene as a model reaction.

2. Experimental

Commercial Nb_2O_5 (CBMM, Brazil) was first activated in air at 500 °C before impregnating it with the active component. Catalyst with 10 wt.% Pd was prepared by impregnating the support with an aqueous solution of palladium nitrate (Aldrich, Analar). The suspension was evaporated to near-dryness on a water bath and air-dried 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 (Ethos 1600, M/s Milestone s.r.l., Italy) at 100% power (650 W, 2.45 GHz) for 5 min (MW catalyst). A temperature of 200 °C was reached in 5 min. The two catalysts were then subjected to reduction at 250 °C in hydrogen before the evaluation. The CH catalyst was also subjected to high-temperature reduction at 450 °C to study its effect on the resistance to deactivation.

Powder X-ray diffraction (XRD) patterns of the CH and MH catalysts were recorded with a Siemens D-5000 X-ray diffractometer using Cu Kα radiation. BET surface area was determined by nitrogen adsorption at −196 °C by the single-point method on the Micromeritics pulse adsorption apparatus. An all-glass, high-vacuum apparatus was used for the determination of hydrogen chemisorption capacities of the catalysts at room temperature (25 °C) using a double isotherm method proposed by Benson et al. [19] and revised by Bonivardi and Beltanas [20] to eliminate the interference of palladium hydride formation. Scanning electron micrographs (SEMs) of the catalysts were obtained in a Hitachi S-520 electron microscope at an accelerated voltage of 10 kV. Samples were mounted on aluminum stubs using double adhesive tape and were gold coated in a Hitachi HUS-5GB vacuum evaporator.

Hydrodechlorination of chlorobenzene was studied in a fixed-bed reactor, at atmospheric pressure, in the

temperature range 140–200 °C, maintaining the hydrogen to chlorobenzene molar ratio at 3:1. Chlorobenzene was fed through a microprocessor-based feed pump at a velocity of 4 ml/h into a glass reactor in which 0.8 g of the catalyst (18/25 BSS mesh size) was suspended between two quartz wool plugs. The reaction product was collected every hour during the time-on-stream (TOS) analysis, carried out over a period of 16 h. The liquid product was analyzed by a gas chromatograph using carbowax 20 M column and FID detector. The product distribution obtained after 6 h of TOS was used for the sake of comparison of catalytic activity.

3. Results and discussion

The BET surface area, hydrogen uptake and the corresponding values of palladium dispersion along with the particle size are presented in Table 1. A considerable decrease in the surface area of the amorphous niobium oxide (145 m^2/g) has been observed after calcination in air at 500 °C (45 m^2/g). The surface area has recorded a substantial decrease after impregnation of the support with palladium, the CH catalyst recording 9 m^2/g and the MW catalyst, 6 m^2/g. The hydrogen uptake is 21 μmol/g in the case of the CH catalyst and in MH catalyst it is 14 μmol/g. The lower values of hydrogen uptake (Table 1) is reflected in lower dispersion with a corresponding increase in particle size. The results are consistent with the observations of Aramendia et al. [21] who have reported lower Pd dispersion with increase in reduction temperature. A close comparison of the XRD patterns of the Nb$_2$O$_5$ support (not shown) with those of the CH catalyst before and after reduction has revealed some important changes in the active phase. Whereas peaks due to palladium oxide are evident in the case of fresh CH catalyst (2θ: 33.9, 54.8 and 60.5°), the reduced catalysts display the transformation of the oxide into

α-Pd (2θ: 40.1 and 46.7°) with increase in peak intensity due to increase of reduction temperature from 250 to 450 °C. There is no indication of formation of any new phase due to interaction of Pd with the support. The MH catalyst also displays similar behavior after low-temperature (250 °C) reduction. Palladium oxide is reduced to palladium metal at temperatures lower than 200 °C and this is known to increase the hydrogen uptake [22,23]. Similar observation were also reported in our previous investigation [7] on Pd/γ-Al$_2$O$_3$ catalyst.

Consolidation of the results obtained by BET surface area, hydrogen chemisorption and XRD analyses reveals that the microwave irradiation facilitates faster removal of water, leads to agglomeration of palladium particles with the consequence of reduction in surface area and the hydrogen uptake. Microwave irradiation is reported to offer moisture leveling during catalyst synthesis. In a solid mass, the pockets of higher moisture content receive proportionately higher extent of radiation and hence dehydroxylation occurs uniformly and at a faster rate compared to its conventional analog, which proceeds, by conduction and convection. This faster dehydroxylation facilitates agglomeration of the palladium metal leading to lower dispersion. The SEM pictures (Fig. 1) obtained on CH and MW catalysts corroborate the results obtained on hydrogen chemisorption. In the case of MH catalyst, agglomeration of Pd into larger particles is clearly visible.

The data obtained from the TOS analyses on MW (reduced at 250 °C) and the CH catalysts (reduced at low temperature, i.e., 250 °C and high temperature, i.e., 450 °C) are shown in Fig. 2. A comparison of the activity data, over a period of 16 h obtained after low-temperature reduction, on the MH and CH catalysts, reveals that whereas the decrease in initial chlorobenzene conversion is only 2–3% in the case of the MH catalyst, it is about 20% in the case of the CH catalyst, which is a significant observation. Further, as the MH catalyst appears to attain steady-state faster,

Table 1
Surface area and hydrogen adsorption values obtained on microwave and conventionally heated catalysts

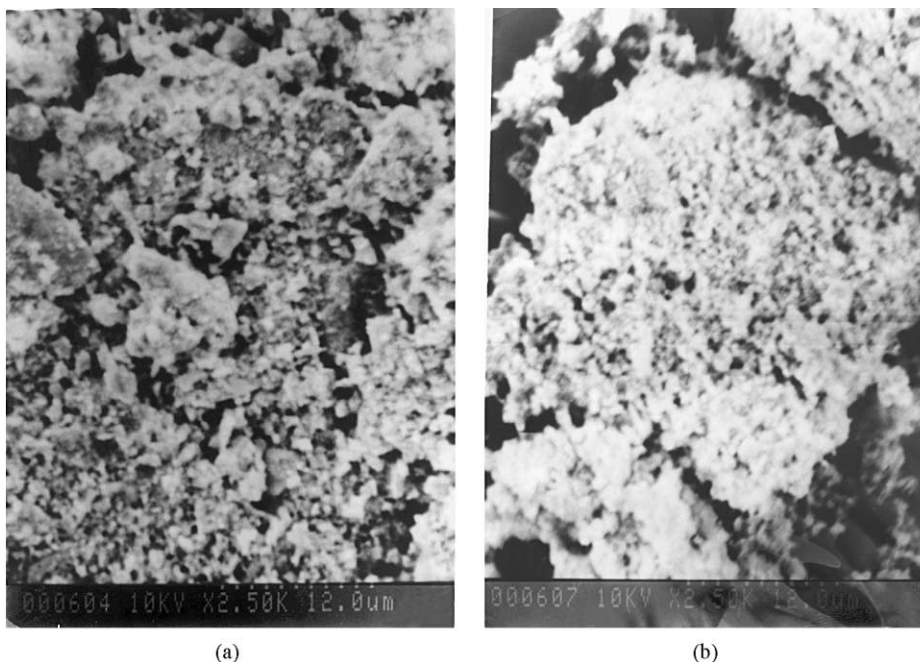|	BET surface area (m^2/g)	Hydrogen uptake (μmol/g)	Pd dispersion (%)	Pd particle size (Å)
Microwave-heated catalyst	6	14	3	377
Conventionally heated catalyst	9	21	4.5	251

Fig. 1. SEM pictures of the fresh Nb_2O_5-supported Pd catalysts: (a) CH catalyst; (b) MH catalyst.

the CH catalyst displays a continual loss in its initial activity. Another important observation from Fig. 2 is that the CH catalyst, after high-temperature reduction (450 °C), shows better resistance to deactivation compared to the catalyst reduced at lower temperature, even though there is a decline in the initial activity after about 6 h of TOS. This phenomenon may be attributed to increase in particle size, possibly by sintering, during reduction at higher temperature. Marginal improvement in the performance of the catalyst during the hydrodechlorination of CCl_2F_2 has already been reported [16]. However, high-temperature reduction has a detrimental effect of interaction of palladium with the support leading to formation of new surface species. Thus, the MH catalyst reduced at low temperature is found to have better resistant to deactivation than the high-temperature reduced conventionally prepared catalyst.

The data obtained on the steady-state chlorobenzene hydrogenolysis activity at two different space velocities (GHSV = 4000 and 32 000 h^{-1}, respectively) are given in Fig. 3. The steady-state residual activity has been consistently high in the case of the

MW catalyst, under both the operating conditions, in the temperature range 140–200 °C.

A comparison of the particle size reported in Table 1 with the activity displayed in Figs. 2 and 3 indicates that the particle size effect is more pronounced in higher activity and resistance to deactivation. Similar observations have also been made in literature. CCl_4 disposal, by its hydrodechlorination to $CHCl_3$, is reported by Zhang and Beard [24] using commercial Pt/Al_2O_3 catalyst. They have proposed that increase in particle size of Pt (achieved by NH_4Cl treatment) is responsible for the resistance to HCl poisoning. Low-dispersed catalysts showing high CH_2F_2 selectivity in Pd/Al_2O_3 is stressed by Malinowski et al. [25]. Aramendia et al. [21], studying the liquid-phase hydrodechlorination of chlorobenzene over Pd catalyst with SiO_2–$AlPO_4$, ZrO_2 and MgO as supports, observed resistance to chlorine deactivation when the size of metallic particle increases. Change in dispersion from 54 to 7% is accompanied by an increase in catalytic activity by a factor of 20.

An important question to be answered at this juncture is how the larger particles offer better resistance
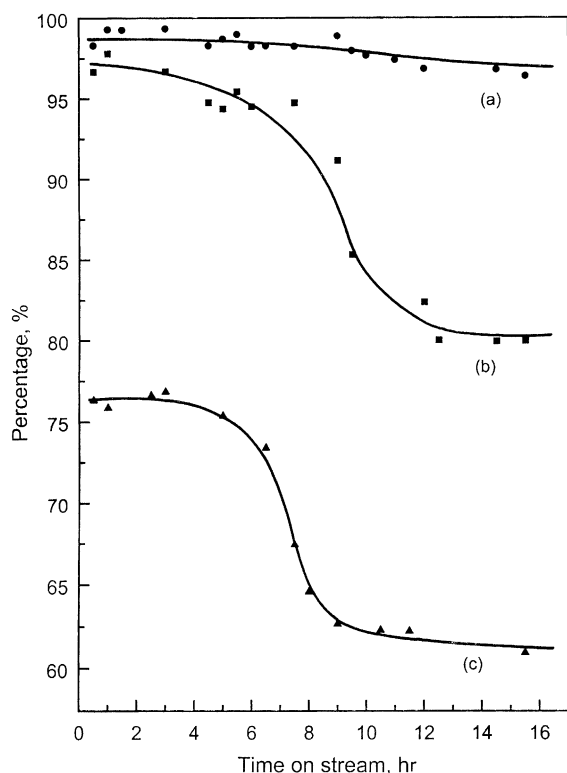
Fig. 2. TOS analyses on the Nb_2O_5-supported Pd catalysts during hydrodechlorination of chlorobenzene: (a) MH catalyst; (b) low-temperature reduced CH catalyst; (c) high-temperature reduced CH catalyst.
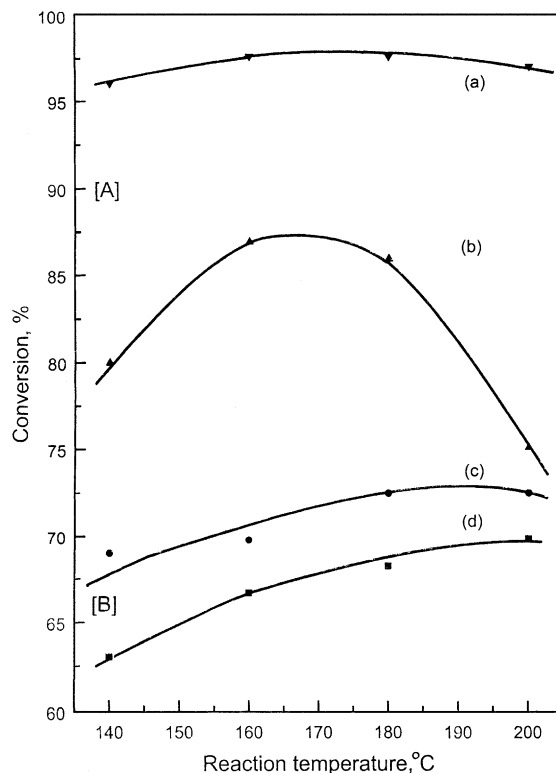

Fig. 3. Variation of residual conversion with the reaction temperature. (A) Space velocity—$4000\,h^{-1}$: (a) microwave-heated catalyst; (b) conventionally heated catalyst. (B) Space velocity—$32\,000\,h^{-1}$: (c) microwave-heated catalyst; (d) conventionally heated catalyst.

to deactivation and effect higher residual conversion. Aramendia et al. [21] propose an explanation for the large particles being more stable towards deactivation. According to them, the larger the Pd particle, the more favorable is the β-PdH formation, which acts as a source of hydrogenation. The ratio ($Pd_{surface}/Pd_{bulk}$) is also high in the case of larger particles offering better resistance to HCl deactivation. However, the stability of β-PdH at higher reaction temperatures, used in this investigation, is questionable. Juszczyk et al. [16] proposed that the facile formation of PdC on the larger particles (with higher proportion of plane atoms) leads to higher selectivity to CH_2F_2. Coq et al. [12] opined that the halide species adsorbed on the metal migrates to the Pd/Al_2O_3 interface to form halogenated species with the support, thus refreshing the metal surface and avoiding gradual passivation of

the catalyst. Though, with the information available, in this investigation, it is difficult to understand the exact mechanism of resistance to deactivation, our results support the preposition that large particles offer more active and better resistant catalysts. Microwave irradiation offers a faster and easy method to prepare catalysts with large Pd particles. Further work on the analysis of the active component at various metal loadings carried out on the catalysts, before and after use in the reaction, could throw more light on this aspect.

4. Conclusion

It may be concluded that microwave irradiation is a fast and an effective technique to obtain catalysts

with large Pd particles which are better resistant to deactivation in hydrodechlorination of chlorobenzene.

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