Catal Lett (2008) 120:312–319
DOI 10.1007/s10562-007-9287-2

Influence of Pd Precursor and Method of Preparation on Hydrodechlorination Activity of Alumina Supported Palladium Catalysts

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Received: 25 June 2007 / Accepted: 27 September 2007 / Published online: 16 October 2007

Abstract A series of alumina supported Pd catalysts were prepared by the novel deposition-precipitation method adopting the chloride precursor (DP-Cl) of Pd and varying the metal content from 0.25 to 1.0 wt%. The catalytic properties of prepared catalysts were studied by various characterization techniques such as N_2 adsorption, CO chemisorption, TPR, XRD, XPS, and TEM techniques. The activity and stability of the catalysts were evaluated for the gas phase hydrodechlorination (HDC) of chlorobenzene operating at atmospheric pressure. At 1 wt% of Pd the catalyst showed higher chlorobenzene conversion with good stability when tested for a period of 25 h, whereas the other catalysts exhibited a loss in activity with time. In order to elucidate the exceptional activity and stability of this catalyst, a few more catalysts with 1 wt% Pd were prepared by impregnation technique and also using a non-chloride precursor, palladium nitrate. The 1 wt% DP-Cl catalyst again was found to be the best among the others. The activity and stability of the DP-Cl catalyst was also found to be superior to two low-dispersed catalysts, each with 10 wt% Pd, prepared by conventional impregnation method using the chloride and nitrate as the precursors. The characterization results reveal that the high activity and stability of the DP-Cl catalyst is related to the formation of electron deficient Pd species and its stabilization in the octahedral vacancies of alumina.

Keywords Hydrodechlorination · Chlorobenzene · Pd/Al_2O_3 catalyst · Deposition–precipitation

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1 Introduction

Chlorinated hydrocarbons (CHCs), which possess unique physical and chemical properties, are extensively used commercially. However, when leaked into the atmosphere they form hazardous pollutants found largely in various waste organic liquids, emissions from a wide range of industrial processes and even in drinking water [1]. Among the various technologies proposed [2, 3] for treating these pollutants catalytic hydrodechlorination is adjudged as a simple, safe, effective methodology, which operates at low temperatures with limited toxic emissions. Among the noble metals, Pd is considered as the best catalyst for selective cleavage of the C–Cl bond [4, 5].

One of the main drawbacks of catalytic hydrodechlorination is the selective adsorption of HCl on the active sites causing deactivation of the catalyst [6]. Many researchers tried various ways to overcome the effect of HCl on the catalysts. A majority of publications suggest usage of low dispersed Pd catalysts (taking 5–10 wt% of metal) on the surface, to obtain stable activity [7–9]. The reasons for high stability of low dispersed catalysts have been variously explained. Coq et al. [10] and Aramendia et al. [7] 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 Pd forming $PdCl_2$. Juszczyk et al. [11] reported that the proportion of surface plane sites is high in the case of larger particles and this phenomenon is responsible for the formation of PdC leading to high selectivity. However, the high cost of Pd has necessitated search for alternate methods of catalyst preparation, for bringing down the Pd content.

$PdCl_2$ is one of the major precursors, which are commonly employed as a source of Pd in the catalyst. The main problem associated with $PdCl_2$ is the presence of residual chlorine on the surface of the finished catalyst, leading to lowering of catalyst activity and stability. The present work aims at identifying a suitable procedure wherein $PdCl_2$ can be effectively used for the preparation of a hydrodechlorination catalyst. Al_2O_3 is chosen as the support for the dispersion of the active component. The applicability of deposition–precipitation method for catalyst preparation is tested. Further, the characteristics of the catalysts, as determined by CO chemisorption, XPS, TPR have been correlated with the activity of the catalysts after identification of the nature of Pd site. The activity and stability of the catalysts are compared with those prepared by conventional impregnation method for the hydrodechlorination of chlorobenzene. The present work is aimed at the development of low Pd (1 wt%) containing, high dispersed catalysts, which are effective and stable for this reaction.

2 Experimental Section

2.1 Catalyst Preparation

In the DP method the support 5 gm of Al_2O_3 was first dispersed into an aqueous solution of $PdCl_2$ (eg: 0.084 g $PdCl_2$ for 1 wt% was dissolved in 5 mL of 1 M HCl) or $Pd(NO_3)_2$. 1 M Na_2CO_3 was slowly added to the palladium solution until the pH value of the mixture reached 10.5. The suspension was then maintained at the same condition for 1h during the precipitation process. The resulting solid was filtered and washed with deionized water several times. A different set of catalysts were also synthesized by conventional impregnation (IMP) on Al_2O_3 with the aqueous solution of metal precursor of required concentration following the wet impregnation method. All the catalysts were then calcined at 500 °C for 5 h in air. The catalysts were designated as DP-Cl, DP-N, IMP-Cl, IMP-N where DP and IMP refer to deposition–precipitation and impregnation methods respectively, Cl and N refer to the chloride and nitrate precursors of Pd, respectively.

2.2 Characterization Methods

XRD patterns were recorded on a Rigaku, D-5000 Diffractometer, by using Ni-filtered CuK_α radiation ($\lambda = 1.5405$ Å). The measurements were recorded in steps of 0.045° with count time of 0.5 s in 2θ range of 10–80°. Identification of the crystalline phases was made with the help of JCPDS files.

Temperature programmed reduction (TPR) of the catalysts were carried out in a flow of 10% H_2/Ar mixture gas at a flow rate of 30 mL/min with a temperature ramp of 10 °C/min. Before the TPR run the catalysts were pretreated in argon at 300 °C for 2 h. The hydrogen consumption was monitored using thermal conductivity detector of a gas chromatograph (Varian, 8301).

CO chemisorption was carried out with a pulse adsorption apparatus at room temperature. In a typical experiment, the catalyst was first oxidized in a 10% O_2/He mixture at 300 °C for 30 min and subsequently reduced in 10% H_2/He gas at the same temperature, flushing with pure He in between. The CO adsorption capacity was then obtained by the number of pulses required to saturate the total surface of the catalyst.

The specific surface areas of the catalyst samples were estimated by using N_2 adsorption at –196 °C by the single point BET method using Micromeritics Pulse Chemisorb 2700. Prior to BET measurement, the samples were dried at 150 °C for 2 h.

XPS measurements were conducted with a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using the MgK_α anode. The non-monochromatized Al-K_α X-ray source ($h\nu = 1486.6$ eV) was operated at 12.5 kV and 16 mA. Before acquisition of the data the sample was out gassed for about 3 h at 100 °C under a pressure of 1.0×10^{-2} torr to minimize surface contamination. The XPS instrument was calibrated using Au as a standard material. For energy calibration, the carbon 1s photoelectron line was used. The carbon 1s binding energy was taken as 285 eV. Charge neutralization of 2 eV was used to balance the charge up of the sample. The spectra were deconvoluted using Sun Solaris based Vision-2 curve resolver. The location and the full width at half maximum (FWHM) value for the species were first determined using the spectrum of pure sample. The location and FWHM of products, which were not obtained as pure species were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general reproducible within ±0.1 eV.

The morphological changes of the catalysts were monitored using a transmission electron microscope, JEOL JEM 2000EXII, operating between 160 and 180 kV. The specimens were prepared by dispersing the samples in methanol using ultrasonic bath and evaporating a drop of resultant suspension onto the lacey carbon support grid.

2.3 Activity Measurements

Hydrodechlorination of chlorobenzene was studied in a fixed-bed micro catalytic reactor (made of pyrex glass, 10 mm inner diameter, 30 cm long) at the temperature of 140 °C and, at atmospheric pressure. In a typical experiment about 0.8 g of catalyst was suspended between two quartz plugs and pre-reduced in a flow of hydrogen (30 mL/min) at 250 °C for 4 h, prior to the reaction. After bringing the temperature of catalyst to the required level, the reactant chlorobenzene was fed at a liquid flow rate of 4.5 mL/h. The hydrogen to chlorobenzene molar ratio was maintained at 3:1. The products were analyzed by a gas chromatograph equipped with a FID detector and a carbowax-20 M column.

The percentage conversion of chlorobenzene was defined as follows,

$$\begin{aligned}&\%\ \text{Conversion of chlorobenzene}\\&\quad = 100\ (\text{moles of chlorobenzene fed} - \text{moles of}\\&\qquad \text{chlorobenzene remaining})/\text{moles of chlorobenzene fed}\end{aligned}$$

3 Results and Discussion

3.1 The Hydrodechlorination Activity of DP-Cl Catalysts: Optimization of Pd Loading

The activity profiles of the catalysts towards chlorobenzene hydrodechlorination are shown in Fig. 1. Hydrodechlorination of chlorobenzene could produces three products, namely benzene, cyclohexane and chlorocyclohexane. However, the formation of either cyclohexane or chlorocyclohexane was not observed in detectable quantities. All the DP-Cl catalysts recorded high initial activity (close to 100%) but their steady state conversion differed after 10 h of reaction. The catalyst having 0.25 wt% Pd showed about 55% conversion. The steady-state conversion increased with increase in loading, reaching higher conversion at 1 wt% Pd loading. Thus, the 1 wt% Pd catalysts achieved the highest stability. As the Pd loading increased, obviously the relative number of active species might have increased, therefore the HDC activity proportionately increased.

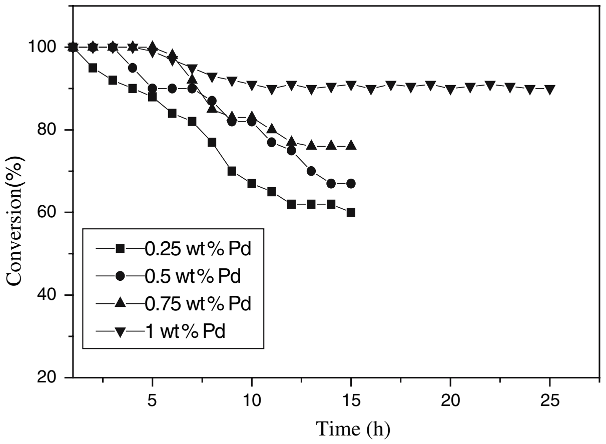


Fig. 1 Time on stream analyses of Al_2O_3 supported Pd catalysts prepared by deposition-precipitation from chloride precursor during hydrodechlorination of chlorobenzene

3.2 Characterization of Low Loaded DP-Cl Pd (0.25–1 wt%) Catalysts

The BET surface area and CO chemisorption results of the catalysts with varying Pd loading from 0.25 to 1 wt% Pd, prepared by deposition–precipitation from chloride precursor, are presented in Table 1. The surface area of ϒ-alumina was found to be 195 m^2/g. As the Pd loading increased from 0.25 to 1 wt%, the BET surface area decreased marginally from 192 m^2/g to 181 m^2/g implying uniform distribution of the active component. The dispersion of Pd, its surface area and particle size were calculated from the corresponding values of CO uptake and are presented in the same table. The CO chemisorption studies revealed that the 0.25 wt% Pd catalyst possessed the highest dispersion of 89% corresponding to a particle size of 1.25 nm. Increase in Pd loading decreased the dispersion to 60% at 1 wt% loading. The corresponding particle size marginally increased to 1.86 nm. High dispersion of Pd catalysts prepared with chloride precursor was the manifestation of a facile formation of a complex species of the form $Pd_xO_yCl_z$ on the alumina surface [12–14].

The XRD patterns (figure not shown) of the DP catalysts (0.25, 0.5, 0.75 & 1 wt% Pd) exhibited peaks due to the diffraction of the support alone. High surface area of alumina support as well as the low metal content (<1 wt%) led to a highly dispersed state of Pd on the support, and therefore the smaller Pd particles could not be detected by XRD analysis.

The TPR profiles of the catalysts with varying Pd content from 0.25 to 1 wt% are shown in Fig. 2. The profiles revealed the information about the variation of reduction temperature of Pd species with respect to Pd loading. Essentially, the catalysts exhibited two types of reduction peaks; one is at lower temperature region (80–200 °C) and the other in the high temperature region (300–400 °C). In the low temperature region, again the reduction temperature of Pd increased gradually as the content of Pd decreased, due to formation of smaller Pd particles as Pd loading decreased. The splitting of the reduction peak in this region can be ascribed to the non-uniform distribution of the particle size, as also reported by Shen et al. [15]. All catalysts exhibited a broad high temperature hydrogen consumption peak centered at 300–400 °C displayed the significance of reduction of two-dimensional PdO surface that interacted strongly with the support. Barrera et al. also

Table 1 Physico-chemical properties of the Pd/Al_2O_3 catalysts prepared by deposition-precipitation method

Sample name	Surface area (m^2/g)	CO uptake (Ncc/g)	Dispersion (%)	Specific metal area (m^2/g)	Particle size (nm)
Al_2O_3	195	–	–	–	–
DP-Cl (1 wt%)	181	1.26	60	2.68	1.86
DP-Cl (0.75 wt%)	180	1.21	77	2.56	1.45
DP-Cl (0.5 wt%)	187	0.86	82	1.82	1.36
DP-Cl (0.25 wt%)	192	0.47	89	0.99	1.25
IMP-Cl (1 wt%)	167	0.55	26	1.16	4.3
DP-N (1 wt%)	147	0.14	7	0.6	16.0
IMP-N (1 wt%)	154	0.13	6	0.5	18.6

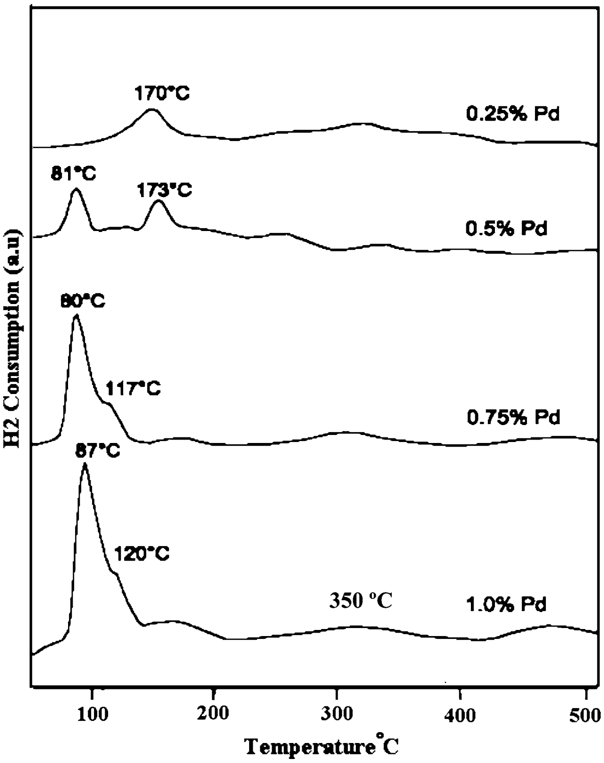


Fig. 2 TPR patterns of Al_2O_3 supported Pd catalysts prepared by deposition-precipitation method

observed such a peak in the case of catalysts with low concentrations of Pd and when consequently the dispersion is high [16]. This is a more stable surface phase.

3.3 Comparison of the Activities of the 1 wt% Catalysts: The Influence of Method of Preparation and the Nature of Pd Precursor

In order to understand the effect of method of preparation and the nature of precursor on the activity, catalysts with 1 wt% Pd were prepared by impregnation as another method of preparation and usage of palladium nitrate as the other precursor.

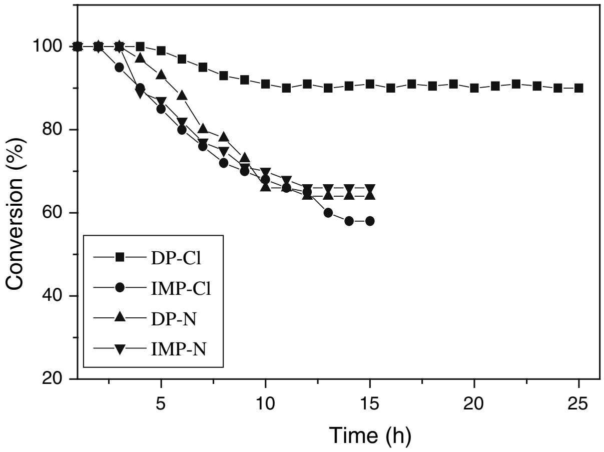


Fig. 3 Time on stream analysis of Al_2O_3 supported Pd catalysts during hydrodechlorination of chlorobenzene

The results of isothermal (140 °C) time on stream analysis of the catalysts, carried out for a continuous period of 15 h, are shown in Fig. 3. The activity results showed that all the catalysts exhibited an initial chlorobenzene conversion of 100%, which also lasted for about 5 h. However, the IMP-Cl, DP-N and IMP-N catalysts recorded continuous decline in their activity reaching a chlorobenzene steady-sate conversion of about 60–65%. The activity of the catalyst at any given time followed the order: DP-Cl > IMP-Cl > DP-N > IMP-N. The DP-Cl catalyst showed nearly 100% chlorobenzene conversion throughout the period of 25 h with out any deactivation.

3.4 Characterization of the IMP-N, IMP-Cl, DP-N and DP-Cl Catalysts

The BET surface area and CO chemisorption results of the catalysts prepared by different preparation methods and Pd precursors are also summarized in Table 1. Among all the catalysts the DP-Cl exhibited the highest surface area of 181 m^2/g and the DP-N was the lowest with 147 m^2/g. This can be attributed to the formation of larger Pd particles inside the pores of the DP-N catalyst, as confirmed by the chemosorption data.

The catalysts prepared from chloride precursor showed higher dispersions compared to their nitrate analogues, as reported in the previous section. The differences in the dispersion are related to the nature of Pd precursor. The metal- support interaction is yet another important factor that contributes to the overall dispersion of the catalysts. Several papers reported higher dispersions for catalysts prepared using $PdCl_2$ precursor than those from chlorine-free precursors in the case of Pd/Al_2O_3 catalysts. The authors thought that dissolution of $PdCl_2$ in HCl forms $PdCl_4^{2-}$, [12, 13] and an anion exchange reaction proceeds between $PdCl_4^{2-}$ and OH^- groups on the alumina surface that might increase the Pd dispersion [12, 17, 18]. As mentioned earlier, in the case of DP-Cl catalysts, a strong chemical bonding of the type, Pd–O–Al is formed at the Pd-support interface during the process of dehydration. This strong interaction inhibits the agglomeration of metal on the surface resulting in a highly dispersed state of Pd.

An interesting observation that can be made from the chemisorption results is that the catalysts prepared by the nitrate precursor showed similar dispersions irrespective of the nature of preparation method. A facile formation of PdO occurs during the preparation, as palladium nitrate is known to decompose easily at lower temperatures. The lower dispersions of the catalysts from nitrate precursor are due to poor interaction between the metal and support [19]. TPR profiles (Fig. 4.) of the catalysts show the hydrogen consumption peaks mainly centered in the region of 50–150 °C. The small hydrogen consumption by IMP-Cl catalyst at 123 °C is related to the resistance to reduction in the presence of chlorine [20]. An important observation is that the intensity of the peak attained its maximum value for the DP-Cl catalyst by converting chlorine content into its hydroxide, from which the PdO forms which can be easily reduced. IMP-N and DP-N catalysts exhibited predominant reduction of PdO to metallic Pd with low peak intensity relatively lower than DP-Cl catalyst. The difference in intensity of H_2 consumption peak might be a manifestation of change in particle size, as reported in Table 1, or an induced salt-support interaction during deposition precipitation. Finally, it was observed that none of the catalysts exhibited the negative peak associated with the decomposition of β-PdH, which is a general characteristic of high Pd containing catalysts.

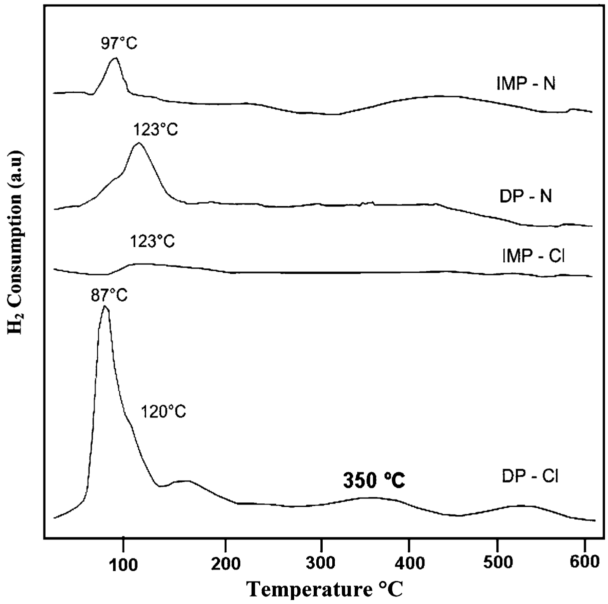


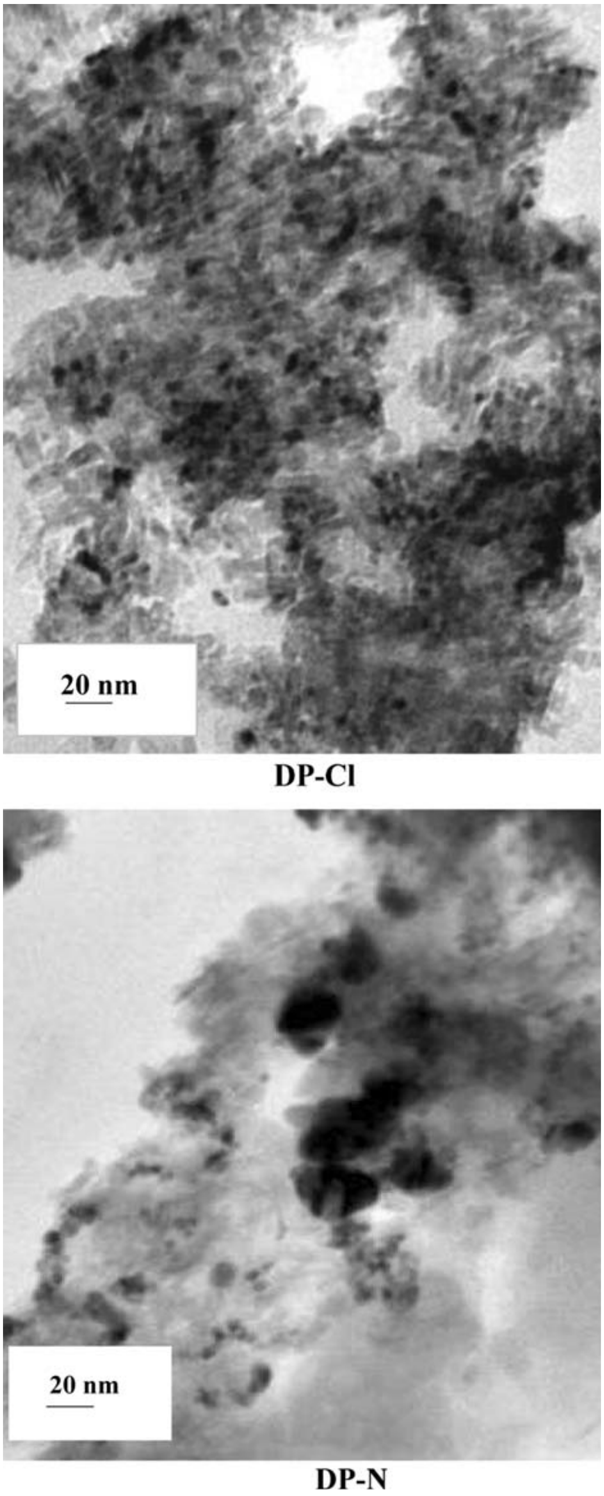
Fig. 4 TPR patterns of Al_2O_3 supported Pd catalysts

TEM micrograph of the DP-Cl catalyst (Fig. 5.) revealed that the average Pd particle size in DP-Cl catalyst is found to be close to the value obtained with CO chemisorption studies. The average particle size of Pd from TEM measurements was found in the range of 2–3 nm. This clearly indicates that during the DP method, the dispersion of Pd is high, which resulted in lower particle size. Whereas, the DP-N catalyst exhibited the formation of larger Pd particles. The TEM measurements also clearly demonstrate that in the DP-Cl catalyst the size distribution of Pd particles is uniform and the average particle size is smaller than the other catalysts.

3.5 Identification of the Nature of Pd Species

The XPS spectra of the reduced 1 wt% Pd DP-Cl, IMP-Cl, DP-N and IMP N catalysts are shown in Fig. 6. The binding energy of Pd $3d_{5/2}$ for metallic Pd is 335.0 eV [21]. In the case of reduced DP-Cl catalyst the shift of Pd $3d_{5/2}$ binding energy to a higher value of 336.5 eV compared to that of metallic Pd suggests the existence of cationic Pd or Pd with a valency close to 1+ [15, 22]. As Al_2O_3 is an interacting support, the strong contact between the Pd and alumina facilitates electron transfer from Pd to Al_2O_3 leading to the formation of cationic Pd on the surface, which is reflected in the increased binding energy on the outer electron shells of the metal. Zhang and Beard [23] also suggested that Pt clusters anchored to Lewis acid sites in alumina form Pt_n (Al) O_3 structures, which contribute to electron deficient character of platinum.

The Pd $3d_{5/2}$ binding energy for the reduced IMP-Cl catalyst was obtained as 337.5 eV. The observed peak maximum for IMP-Cl catalyst indicates the presence of a complex species, $PdCl_4^{2-}$, as well as $PdCl_2$. The XPS results indicate that alumina supported palladium catalysts synthesized by impregnation method retain chlorine on its surface even after reduction at 300 °C [13].



DP-Cl

DP-N

Fig. 5 TEM micrographs of reduced Al_2O_3 supported Pd catalysts

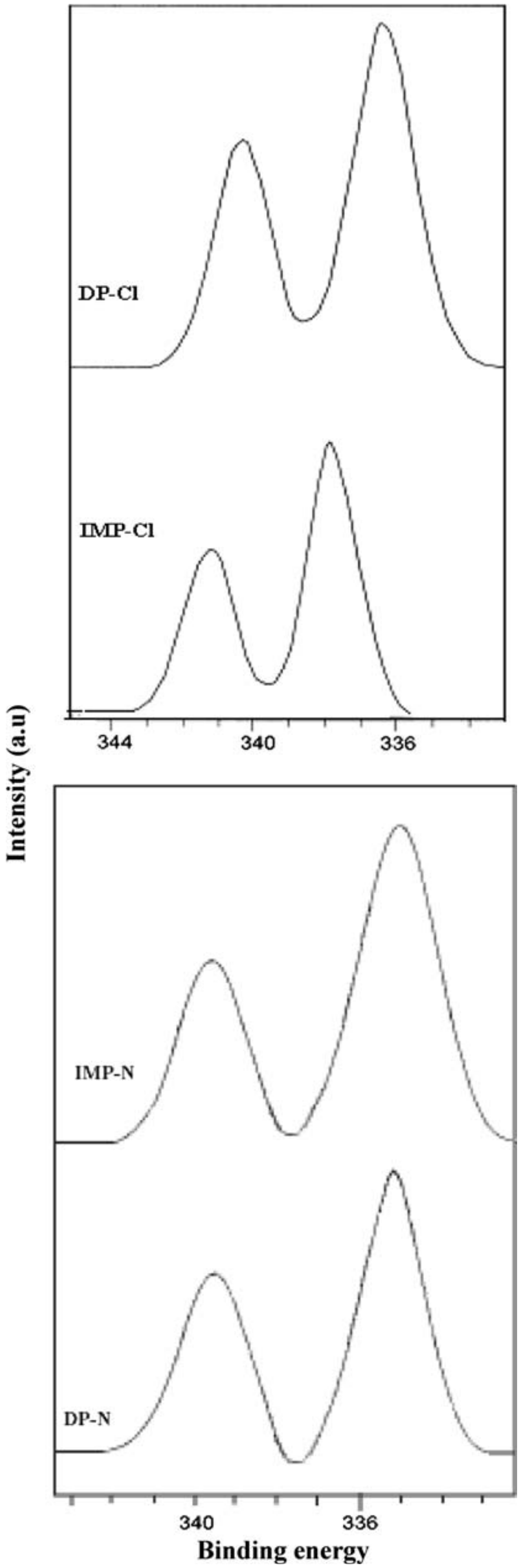


Fig. 6 XPS spectra of reduced Al_2O_3 supported Pd catalysts

IMP-N and DP-N catalysts exhibited B.E values for Pd $3d_{5/2}$ as 335.2 and 335.3 eV respectively. These values are close to the B.E of metallic Pd $3d_{5/2}$ clearly demonstrating that the catalysts prepared from nitrate precursor of Pd results into weak metal-support interaction irrespective of the method of catalyst preparation.

3.6 Comparison of the Catalytic Activities of the 1 wt% DP-Cl Catalyst with the Conventional 10 wt% Pd Catalysts

In order to reiterate the novelty of catalyst, a comparison of the data obtained during the time on stream analyses on the catalysts was made in Fig. 7 between the 1 wt% Pd DP-Cl and the 10 wt% Pd catalysts. The latter catalysts were prepared by impregnation method using the chloride and nitrate precursors of Pd. It can be observed that the 1 wt% Pd DP-Cl catalyst is more active and stable than the conventional 10 wt% Pd catalysts.

3.7 The Versatility of 1 wt% DP-Cl Catalyst

The variation in the chlorobenzene conversion can be explained based on the catalyst characterization by XPS, CO chemisorption, TEM, BET surface area and TPR studies. The variation in catalytic activity of DP-Cl catalysts with different Pd loadings observed in Fig. 1 could be related to the relative propensity of the cationic Pd sites. It appears that the number of these sites attains maximum at 1 wt% of Pd on the support surface.

The 1 wt% Pd catalysts, all of them had high initial activity, which means that Pd, in its partially or fully reduced form, is active for hydrodechlorination. However, the difference in stability among the catalysts can be explained in terms of the nature of the active species. Pd in its metallic form gets deactivated faster by chlorine attack forms $PdCl_2$ whereas the Pd in DP-Cl catalyst is does not.

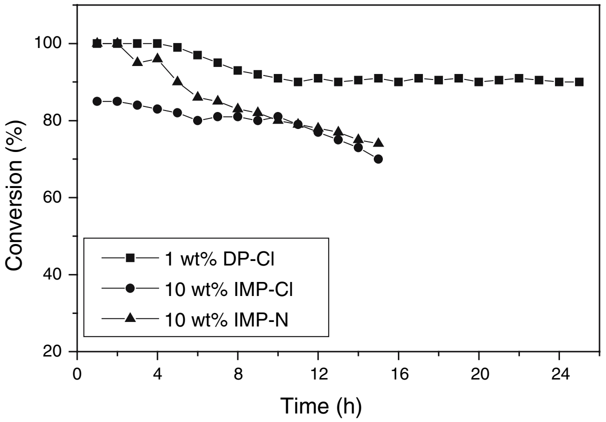


Fig. 7 Comparison of the time on stream analysis of 1 wt% Pd DP-Cl catalyst and 10 wt% Pd catalyst during the hydrodechlorination of chlorobenzene

The existence of Pd in the cationic form appears to be responsible for the higher activity and stability. Literature studies have revealed better performances of the catalysts containing cationic Pd species. The interaction of Pd with zeolite Y [24] (or) Al_2O_3 [25] led to the formation of electron—deficient metal species. The essential role of Pd^{n+} ions in catalyzing the production of methanol from synthesis gas was demonstrated by Ponec et al. [26]. Similarly, Pd^{1+} ions (in PdX zeolites) were identified as active species in the dimerization of ethylene [27]. Berry et al. [9] studied the hydrodechlorination activity of microwave irradiated PdO/Al_2O_3 catalysts and the high activity of the catalysts are correlated with the occurrence of Pd^{n+} ion.

An important question that needs to be answered at this juncture is how the existence of Pd^{n+} offers high activity and also stability to the catalysts. A few explanations can be thought off to arrive at a conclusion. Alumina unlike other supports, has unoccupied octahedral sites and therefore if we assume that on the surface of Al_2O_3 the top O^{2-} ion of the octahedron is missing, the remaining part of O^{2-} skeleton forms a square pyramid. Juszczyk et al. [28] reported that alumina stabilizes Pd^{n+} ion in these vacant octahedral holes. Therefore, the stabilization of the cationic Pd appears to be more favorable on alumina.

Alternatively, in the hydrodechlorination reaction two major reactions are prominent:

(i) The oxidative addition of chlorobenzene on the Pd surface forming palladium chloride, followed by the elimination of benzene (chlorination), and
(ii) The regeneration of metal surface by hydrogen (hydrogenation).

Since chlorination is favorable on both metallic as well as cationic Pd, those catalysts which have higher rate of hydrogenation than that of chlorination exhibit better stability. It appears that the DP-Cl catalyst, containing the Pd^{n+} ions, enhances the rate of hydrogenation substantially. Consequently, it leads to enhancement in the hydrodechlorination stability.

Another explanation can also be offered taking into account the electronic property of cationic Pd. The smaller electron deficient Pd particles are more resistant to chlorine adsorption than the larger ones. Chlorine is strongly adsorbed on large metal particles, which show high electron density. On the other hand, in smaller Pd particles the chlorine is weakly adsorbed due to the electron deficient character of Pd [9, 27]. Thus the DP-Cl catalyst which exhibit electron deficient Pd offers considerable resistance to the deactivation by HCl poisoning.

The regeneration of chlorine adsorbed cationic Pd, during the hydrodechlorination reaction, could also be another reason for higher stability of the DP-Cl catalysts.

Table 2 XPS analysis of Pd/Al_2O_3 catalysts

Catalyst	Pd $3d_{5/2}$ B.E (eV)	Pd 3d/Al 2p	Cl 2p/Pd 3d
DP-Cl	336.5	0.67	Traces
IMP-Cl	337.5	0.44	3.7
DP-N	335.3	0.48	–
IMP-N	335.2	0.51	–

TEM pictures also gave an evidence for the formation of smaller Pd particles in case of DP-Cl catalyst. Conversely, the activity of low loaded Pd catalysts (0.25 to 0.75 wt%) is continually declined though having smaller particle size at than 1 wt% DP-Cl. It implies that, a balance between an extent of Pd^{n+} formation and particle size is perceptive to achieve greater stability of the catalyst. It appears that in the hydrodechlorination of C–Cl bond, the chlorine atoms liberated and subsequently transported to the Al_2O_3 lattice by surface diffusion, thus transforming it at least partially into a more active $AlCl_3$ species. The presence of $AlCl_3$ species at the Pd-Al interface induces the regeneration of electron deficient species that are active for hydrodechlorination reaction. Coq et al. [29] suggested that during the CCl_2F_2 hydrodechlorination the presence of electron-deficient Pd species which were generated in the close proximity of ϒ-alumina. The support was modified by the fluorine species into an AlF_x form. A similar explanation seems to hold good in the present case as well.

4 Conclusions

In summary, a loading of 1 wt% Pd on Al_2O_3 appears to be the optimum for attaining high activity and stability for the DP-Cl catalysts, as the number of active Pd sites created reached a maximum at this loading. Effective removal of excessive chlorine from the surface by adopting deposition precipitation leads to a strong interaction between the metal and the support, leading to the formation of Pd^{n+} ions and their stabilization on the alumina surface appears to be the main reason for the excellent performance of the catalyst (Table 2).

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