

A highly active low Pd content catalyst synthesized by deposition–precipitation method for hydrodechlorination of chlorobenzene

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Abstract

Hydrodechlorination (HDC) of chlorobenzene was tested over 1 wt.% Pd supported on ZrO₂ synthesized by deposition–precipitation (DP) and conventional impregnation (IMP) methods. The effect of precursor was also investigated using chloride and nitrate salts of Pd. The catalysts were characterized by CO chemisorption, BET surface area, XPS, and temperature-programmed reduction (TPR). The catalyst prepared by the DP method using chloride precursor has shown the highest activity and stability compared to the other catalysts. The variation in chlorobenzene conversion of different catalysts is explained based on the nature of Pd species formed on the surface. A comparison of the HDC functionality of the most stable 1 wt.% catalyst with that of a 10 wt.% catalyst, prepared by the conventional impregnation method, has been made. In contrast to the general observation that the low dispersed catalysts are preferred for hydrodechlorination, it is noted that the high-dispersed catalysts prepared by the DP method offer better performance. This is a significant observation in terms of considerable reduction in palladium content and the availability of more active surface area.

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1. Introduction

Catalytic hydrodechlorination (HDC) has emerged as a promising non-destructive technology not only for the safe conversion of chlorinated waste, but also producing value-added products [1–4]. Among all Group VIII noble metals, Pd is identified as the best metal for HDC since it selectively replaces chlorine of the substrate with hydrogen ion [5–8].

Catalysts employed for HDC reaction are often susceptible for deactivation, due to strong adsorption of HCl produced as a by-product. In this context, the development of a poison-resistant catalyst has gained significant importance

in recent years. The hydrodechlorination activity depends on the nature of Pd active sites, which are influenced by several factors such as the method of preparation, the mean particle size and the nature of precursor salt used in the preparation of catalysts. Many researchers have focused their attention on developing stable Pd catalysts using high metal loading (up to 10 wt.%) thereby obtaining catalysts of low Pd dispersion [9,10]. The reasons for high stability of low dispersed catalysts have been variously explained. Aramendia et al. [11] reported that large particle size offers better resistance to HCl deactivation. Juszczak et al. [12] explained the stability phenomenon in terms of formation of PdC on large particles.

However, considerations like the high cost of Pd and the concomitant loss of active surface area at higher loading prompted the search for alternate methods of catalyst

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preparation and investigations into low cost catalysts. The carbothermal method employed by Lingaiah et al. [13] is limited to only carbon-based catalysts. George and Keane [14] successfully used Ni-based catalysts, but these catalysts are better active only at higher temperatures. Hence there is a strong need for the development of low Pd content catalysts with high activity and stability.

Different salts have been used as precursors in the preparation of Pd catalysts employed in the HDC reaction. Catalysts prepared using the chloride precursor are considered not suitable due to the existence of residual chlorine on the surface that block the active sites required for the reaction [15,16]. However, Pd catalysts prepared by DP method, with chloride precursor, have been successfully employed for methanol decomposition [17]. Besides, zirconium oxide has been considered as one of the active supports for Pd when the catalyst is prepared by DP method [18]. Hence, it is interesting to elucidate the applicability of this method in the development of high-dispersed Pd catalyst for the HDC reaction.

In the present investigation, an attempt has been made to prepare ZrO₂ supported 1 wt.% Pd catalysts by the DP as well as conventional IMP methods employing PdCl₂ and Pd(NO₃)₂ as precursors. A comparison is made between the HDC functionality of these catalysts in terms of activity and stability. The results are interpreted based on the nature of Pd species formed on the surface of the catalyst.

2. Experimental

2.1. Catalyst preparation

In the DP method palladium hydroxide was exclusively precipitated by the addition of 1 M Na₂CO₃ on ZrO₂ (Zircon, India) from the uniformly dispersed metal precursor (Pd(NO₃)₂ or PdCl₂) [19]. The pH of the solution was maintained at 10.5 for 1 h during the precipitation process. The resulting solid was filtered, washed with deionized water several times (till no chloride ion was detected by silver nitrate solution), and oven dried at 120 °C for 3 h. A different set of catalysts was also synthesized by the impregnation of ZrO₂ with the aqueous solution of metal precursor of required concentration following the wet impregnation method. The suspension in this case was first evaporated to near dryness on a water bath and then dried in an air oven at 120 °C for 12 h. All the four catalysts were calcined at 500 °C for 5 h. The Pd content in all the catalysts synthesized was uniformly fixed at 1 wt.%. The catalysts were designated as DP-Cl, DP-N, IMP-Cl, and IMP-N where DP and IMP refer to deposition–precipitation and impregnation methods respectively, and Cl and N refer to the chloride and nitrate precursors, respectively. A 10 wt.% Pd supported on ZrO₂ catalyst was also synthesized by the conventional impregnation method as described above for the sake of comparison.

2.2. Catalyst characterization

Room temperature CO chemisorption was carried out on a pulse adsorption apparatus. In a typical experiment, the catalyst was first oxidized in a 10% oxygen/helium mixture at 300 °C for 30 min and was subsequently reduced in a 10% hydrogen/helium mixture under similar conditions with intermittent flushing with pure helium. The CO adsorption capacity was then obtained by the number of pulses required to saturate the surface. BET surface area was determined by nitrogen adsorption at liquid nitrogen temperature. The X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was carried out using a Kratos Axis 165 ESCA spectrometer with a Mg K α source. The catalysts were reduced at 300 °C prior to the XPS analysis. Temperature-programmed reduction (TPR) of the catalysts was performed using 5% hydrogen balanced with helium at a heating rate of 10 °C/min and a gas flow rate of 50 ml/min in the temperature range of 25–600 °C.

The HDC reaction was performed at atmospheric pressure in the temperature range of 140–200 °C. In a typical experiment about 0.8 g of catalyst was suspended between two quartz wool 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 the catalyst to the required level, the reactant chlorobenzene (S.D. Fine-chem Ltd., India, Analar grade) was fed at a liquid flow rate of 4 ml/h by means of a microprocessor based feed pump (Braun Corp., Germany) maintaining a hydrogen to chlorobenzene molar ratio of 3:1. The products were analyzed by gas chromatography using a FID detector and a 10% carbowax 20 M column.

3. Results and discussions

In the present investigation HDC of chlorobenzene resulted in the production of benzene only as the organic product even though there is a possibility for the formation of cyclohexane and chlorocyclohexane as the major and minor by products. The time on stream analysis of the catalysts are shown in Fig. 1. Among all the catalysts, the DP-Cl catalyst has shown the highest chlorobenzene conversion with higher deactivation stability. The activity of the catalysts can be rated as DP-Cl > DP-N \approx IMP-Cl > IMP-N. The catalysts DP-N, IMP-Cl, and IMP-N have shown rather a continuous decline in activity with time. The high activity of the DP-Cl catalyst could be attributed to its high BET surface area and the availability of more number of surface Pd species on ZrO₂. The DP-Cl catalyst has the highest dispersion among all the catalysts. This high value suggests that the precursor greatly influences the dispersion. Ito et al. [22] have also observed higher dispersions for Pd/Al₂O₃ prepared from PdCl₂ precursor.

It needs to be understood how the DP-Cl catalyst offers high Pd dispersion. Fig. 2 represents the TPR patterns of the catalysts. The DP-Cl catalyst exhibits two H₂ consumption peaks at 147 and 466 °C. The DP-N, IMP-Cl and IMP-N

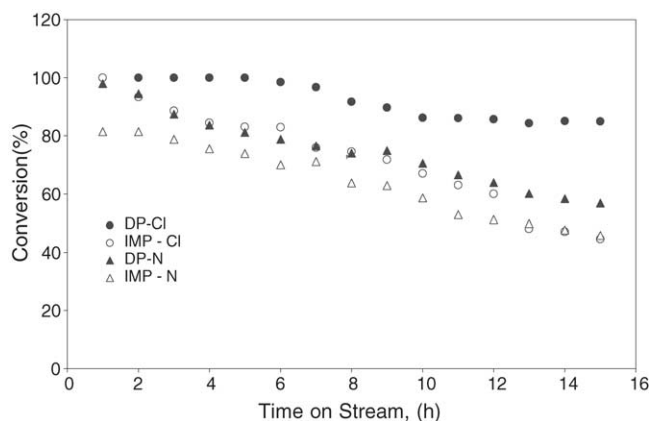


Fig. 1. Time on stream analysis of the catalysts during the hydrodechlorination of chlorobenzene at 140 °C.

catalysts have shown only one consumption peak with their maxima at 172, 127, and 133 °C, respectively. The negative peak corresponding to the decomposition of PdH, normally observed in the case of low dispersed catalysts, is not observed in these high-dispersed catalysts. The low temperature peak obtained in all the catalysts is due to the reduction of less strongly interacted PdO species. The TPR profiles suggest that the Pd species in the catalysts synthesized by DP method reduces at higher temperature irrespective of the precursor. The high temperature peak observed at 466 °C in the case of DP-Cl may be due to the hydrogen consumed by the strongly interacted PdO species at the interface between the metal and the support. As reported by Shen et al. [20] smaller PdO particles that interact strongly with the metal oxide supports are more resistant to reduction. The total amount of H₂ consumed during the TPR analysis along with other physico-chemical properties is also summarized in Table 1. The DP-Cl catalyst has the highest hydrogen consumption compared to the remaining three catalysts.

Low values of Pd dispersion for catalysts synthesized from palladium nitrate may be due to the facile formation of loosely bound PdO during the preparation, as palladium nitrate is

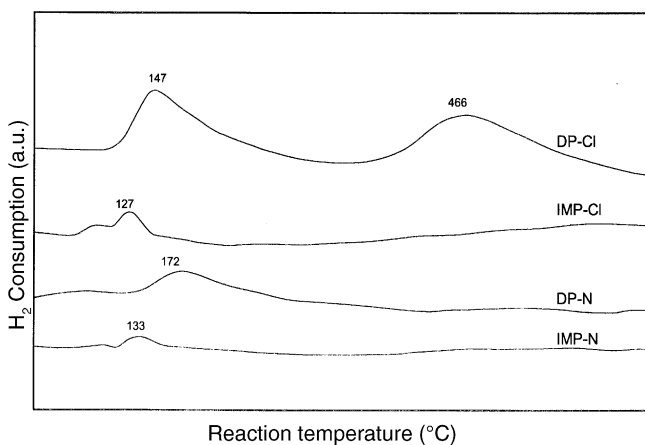


Fig. 2. TPR profiles of Pd/ZrO₂ catalysts.

Table 1
Physico-chemical properties of the Pd/ZrO₂ catalysts

Catalyst	Surface area (m ² /g)	Dispersion (%)	Specific metal (m ² /g)	Particle size (Å)	Total hydrogen consumption (mol/g cat.)
ZrO ₂	55	–	–	–	–
DP-Cl	43	72	6.2	13.4	6.7 × 10 ⁻⁴
IMP-Cl	37	47	4.0	20	9.7 × 10 ⁻⁵
DP-NO	32	8	0.7	117	8.6 × 10 ⁻⁵
IMP-NO	30	7	0.6	127	3.0 × 10 ⁻⁵

known to decompose easily comparatively at lower temperatures than that of palladium chloride.

Fig. 3 shows a comparison of time on stream analysis data between the 1% Pd DP-Cl and the 10 wt.% Pd catalyst prepared by impregnation method during the HDC of chlorobenzene. It can be observed that the 1% Pd DP-Cl catalyst is more active and stable than the 10% Pd IMP-Cl catalyst, reiterating the importance of method of preparation.

The surface analysis of the DP-Cl, IMP-Cl catalysts carried out by XPS, after reduction at 300 °C are shown in Fig. 4. The Pd 3d_{5/2} peaks were closely overlapped by the peaks of Zr 3p both for DP-Cl and IMP-Cl catalysts making the interpretation difficult based on the 3d_{5/2} peaks. However, the Pd 3d_{3/2} peaks for DP-Cl, IMP-Cl are observed at 341.4 and 340.2 eV, respectively. The unresolved peak consisting of Pd_{3/2} and O 1s is deconvoluted and the binding energy (BE) values of Pd 3p_{3/2} and O 1s for DP-Cl catalysts are identified as 533.0 and 532.1 eV, respectively (figure not shown). Similarly for the IMP-Cl catalyst the values for Pd 3p_{3/2} and O 1s are observed at 532.0 and 530.4 eV, respectively. Matsumura et al. [17] reported similar values for the catalysts prepared by the DP and IMP methods. The higher binding energy values obtained for Pd 3d_{3/2} and Pd 3p_{3/2} indicate the formation of cationic Pd species in the DP-Cl catalyst. The XPS results are in agreement with those of Kapoor et al. [21].

The differences in the activity of the 1 wt.% catalysts towards HDC of chlorobenzene can be interpreted based on the experimental results obtained from TPR, XPS and CO

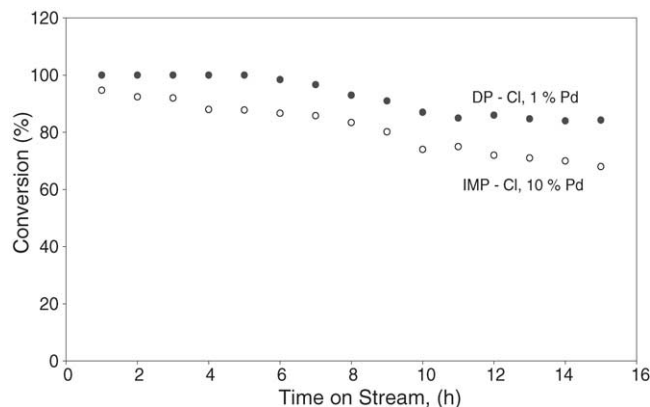


Fig. 3. Comparison of the time on stream analysis of 1% Pd DP-Cl catalyst and 10% Pd IMP-Cl catalyst during the hydrodechlorination of chlorobenzene at 140 °C.

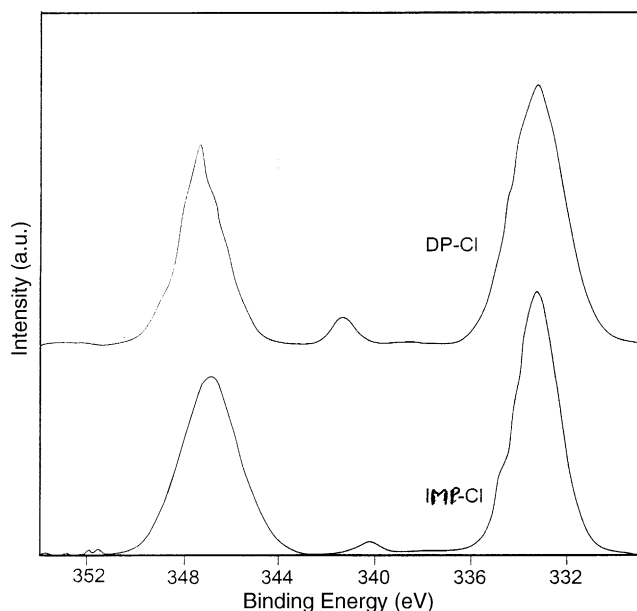


Fig. 4. XPS spectra of the catalysts obtained after reduction at 300 °C.

chemisorption studies. The metal precursor and preparation conditions are known to affect the catalytic activity of supported metal catalysts. The higher activity of DP-Cl catalysts are explained based on the metal–support interactions and its influence on modifying the Pd surface structure. Pd supported on zirconia is known to exhibit metal–support interaction when synthesized by the DP method [17]. The TPR profile of the DP-Cl catalyst in Fig. 2 has shown an additional H₂ consumption peak at 466 °C which may be attributed to the reduction of interfacial PdO species. The total H₂ consumption in DP-Cl catalysts is due to PdO reduction as well as ZrO₂ surface reduction. It seems that Pd promotes the reduction of ZrO₂ as the peak maximum was observed at lower temperatures in the case of DP-Cl catalyst. The high dispersion values for DP-Cl catalyst also support the strong interaction between Pd and ZrO₂.

It is thought that the strong interaction between Pd and support facilitates an easy electron transfer from Pd to Zr producing the cationic Pd species. The XPS results also support the formation of cationic Pd species in DP-Cl catalyst due to high BE of Pd 3d_{3/2} and Pd 3p_{3/2} compared to that of IMP-Cl catalyst. The higher binding energies of O 1s observed for DP-Cl catalysts compared to that of the IMP-Cl suggests that the surface oxygen strongly interact with Pd. The hydroxyl groups on the surface of the support seem to be responsible for the interaction leading to high BE because the DP-Cl catalysts were prepared in an alkaline medium.

The formation of cationic Pd species at the Pd–support interface and their catalytic functionality has been reported by several authors [20]. Le Normand et al. [23] expressed their opinion that the presence of Pd in the cationic form enhances the hydrogenation rate. High activity of the catalysts forming cationic Pd species is also reported in the case of methanol

synthesis from CO and H₂ [20]. The strong interaction of Pd with Zr appears to inhibit the selective adsorption of HCl on Pd thereby holding the active Pd sites intact leading to higher stability of the catalysts. An alternative explanation can also be given for the high stability of DP-Cl catalyst. Two reaction steps are prominent in the HDC reaction. The interaction of chlorobenzene with the metal surface forming a metal chloride (chlorination) with the simultaneous formation of products and the regeneration (hydrogenation) of the metal surface by hydrogen. It appears that the formation of cationic Pd sites in the case of DP-Cl catalyst increases the rate of hydrogenation step substantially.

The lower activity in the case of IMP-Cl catalyst is related to the existence of residual chlorine on the catalyst surface thus blocking the number of accessible Pd sites. The chlorine atoms are hard to be eliminated from the surface even after calcination at 500 °C [24]. The possibility of residual chlorine hindering the metal–support interaction cannot be ruled out. The catalysts prepared using nitrate precursor of palladium shows a decrease in the activity with time even for the catalyst prepared by DP method. The DP-N and IMP-N catalysts have low Pd dispersion irrespective of the method of preparation. It is assumed that there is a facile formation of PdO during the preparation as Pd (NO₃)₂ is known to decompose easily at lower temperature and during the calcination process the agglomeration of Pd metal leads to lower dispersions leading to the reduction in interactions between Pd and ZrO₂. In the case of DP-Cl catalysts it is thought that the strong binding such as Pd–O–Zr takes place at the metal–support interface during the dehydration process and therefore the strong Pd and support interaction inhibits the agglomeration of metal on the surface.

TPR analysis of IMP-Cl, DP-N, and IMP-N catalysts gave only one hydrogen consumption peak related to the reduction of PdO to metallic Pd. There is no H₂ consumption peak at higher temperatures as observed for DP-Cl catalyst suggesting the absence of interaction between metal and support in these catalysts. The absence of such kind of strong interaction may also lead to selective adsorption of HCl on Pd resulting in earlier deactivation of the catalysts.

4. Conclusions

A catalyst synthesized by deposition–precipitation method employing chloride precursor of Pd was effectively used for hydrodechlorination. In DP-Cl catalyst the strong interaction between Pd species and the support not only leads to active cationic Pd species but also inhibits the selective adsorption of HCl leading to higher stability and activity.

Contrary to general expectation that a high Pd content in the catalysts were necessary for hydrodechlorination, the DP catalyst with chloride precursor not only offers better performance but also a substantial reduction in the Pd content was achieved.

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