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Influence of particle size and nature of Pd species on the hydrodechlorination of chloroaromatics: Studies on Pd/TiO_2 catalysts in chlorobenzene conversion

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ABSTRACT

TiO_2 supported Pd catalysts were synthesized by two different preparation methods namely conventional impregnation (IMP) and deposition-precipitation methods (DP) using two precursor salts $Pd(NO_3)_2$ and $PdCl_2$. The catalysts were characterized by various techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), temperature programmed reduction (TPR), CO chemisorption and BET surface area. The catalysts were evaluated for the gas phase hydrodechlorination (HDC) of chlorobenzene (CB) operating at atmospheric pressure. The catalyst prepared by deposition-precipitation using the chloride precursor (DP-Cl) exhibited higher dispersion and different electronic properties compared to the other catalysts. It also exhibited exceptional hydrodechlorination activity and stability. The generation of active electron deficient Pd species (Pd^{n+}) on the catalyst surface appears to be the main reason for this behavior.

1. Introduction

Aromatic chlorocarbons are among the most widespread and persistent toxic pollutants. Consequently, an efficient process for their destruction would be of greater significance. Several methods like incineration, reduction by transition metal activated alkali metal hydrides [1,2], biodegradation [3–5], photocatalytic oxidation [6–8] have been developed for this purpose. However, catalytic hydrodechlorination (HDC) is found to be the most effective method for their safe destruction. It excludes the formation of more toxic compounds such as dioxins, besides being applicable to waste with any content of chlorine. The hydrocarbon produced can be recovered and recycled, thereby the process becomes economical [9].

Noble metals have been identified as promising catalysts for the hydrogenolysis of CHCs [10,11], and among them Pd is considered to be most effective [12–15] as it can operated at low temperature and at atmospheric pressure. HDC proceeds with the liberation of HCl with consequent deactivation of active sites. Catalysts prepared with high Pd content (containing large Pd particles) are shown to exhibit better stability due to easy diffusion of the chloride ion [12,16–18] or formation of PdC [19]. A close look at the literature relating to self-poisoning by the halogen [20–22] reveals that $PdCl_2$ leaves residual chlorine on the surface, necessitating development of new methods for catalyst preparation. Many researchers focused on chlorine-free precursors such as palladium nitrate, which decompose easily into PdO during calcination treatment. The high cost of Pd and the concomitant loss of active surface area at higher loadings are considered to be important factors that needed reduction in Pd content. Gopinath et al. [21] claimed that by adopting the deposition-precipitation method (DP), even highly dispersed Pd catalysts also are equally effective.

The catalytic behavior of Pd depends on the type of the support as well. The extent of interaction between the support and the metal precursor depends upon the ionic charge of the precursor and the isoelectric point (IEP) of the support. In this context, it is interesting to understand the nature of Pd species formed during the preparation of TiO_2 supported Pd catalysts using the DP method. The present work aims at understanding the nature of Pd species and their influence on the activity and stability of the catalyst for HDC of chlorobenzene (CB) when different preparation methods and precursor are used.

2. Experimental

2.1. Catalysts preparation

Titania (Aldrich, S.A.: 48 m^2/g) supported Pd catalysts were prepared using two different precursors namely $Pd(NO_3)_2$ and $PdCl_2$, and by adopting conventional impregnation (IMP) and deposition-precipitation (DP) methods. The composition of Pd metal was fixed at 1 wt.% in all the catalysts. In the conventional impregnation method, aqueous metal precursor solution was dispersed on TiO_2 support and excess of water was evaporated on a water bath followed by oven drying for 12 h at 120 °C. In the deposition-

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precipitation method, the support was suspended in the aqueous solution of the precursor salt and $Pd(OH)_2$ was exclusively precipitated on the support by the slow addition of 1 M Na_2CO_3 solution until the pH of the solution reached a value of 10.5, and keeping the catalyst mass for 1 h in the basic medium. The resultant solid was filtered and washed with deionised water several times until no chloride ion was detected in the filtrate as confirmed by $AgNO_3$ test. The solid thus obtained was oven dried at 120 °C for 6 h and calcined at 500 °C for 5 h. The prepared catalysts are referred to as IMP-N, IMP-Cl and DP-N, DP-Cl (where N represents the nitrate precursor and Cl, the chloride precursor of Pd).

2.2. Characterization of catalysts

XRD patterns were recorded on a Rigaku Diffractometer, by using Ni-filtered Cu Kα radiation (λ = 1.5405 Å). Identification of crystalline phases was made with the help of the JCPDS files. The specific surface areas of the catalyst samples were estimated using N_2 adsorption at −196 °C by the single point BET method using Micromeritics Chemisorb 2700. Room temperature CO chemisorption was carried out on a pulse adsorption apparatus. 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 under similar conditions 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. Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 10% H_2/Ar mixture gas flowing at a 30 ml/min with a temperature ramp of 10 °C/min. Before the TPR run the catalysts were pretreated with argon at 300 °C for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector. XPS measurements were conducted with a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using the Mg Kα anode. Before acquisition of the data the sample, was out gassed for about 3 h at 100 °C under a pressure of 1.0×10^{-7} torr to minimize surface contamination. The other details are available elsewhere [21]. 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

The catalytic activity of TiO_2 supported Pd catalysts was evaluated at 140 °C. In a typical experiment, 0.8 g of catalyst was suspended between two quartz wool plugs and reduced in a flow of hydrogen at 300 °C for 2 h prior to the reaction. After bringing the temperature of the catalyst bed to the required level, the reactant, chlorobenzene (S.D. Fine Chem., AR grade) was fed at a flow rate of 4 ml/h by means of a microprocessor based feed pump (Braun Corp., Germany). The H_2 flow was kept at a molar ratio of H_2 to CB as 3:1. The products were analyzed by gas chromatography using a FID detector.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The XRD patterns of TiO_2 supported Pd catalysts are shown in Fig. 1. The existence of anatase phase of TiO_2 was observed. Besides, there was a slight indication of the formation of the PdO phase with a line at 2θ = 33.5° (JCPDS data base) in all the catalysts. The XRD patterns of reduced catalysts Fig. 2 showed metallic Pd phase (α-Pd at 2θ 40.9°) in the cases of IMP-N, DP-N and IMP-Cl catalysts, and it was absent in DP-Cl catalyst. This implies that the Pd in the first three catalysts was in an easy reducible state whereas that in DP-Cl was not Fig. 2.

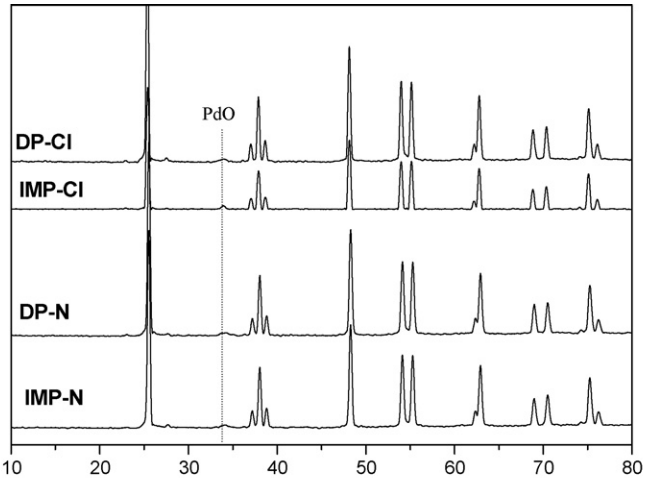

Fig. 1. XRD patterns of unreduced TiO_2 supported Pd catalysts.

3.2. BET surface area

The physico-chemical properties of Pd/TiO_2 catalysts are presented in Table 1. The surface area of TiO_2 support was measured as 48 m^2/g. The surface areas of the catalysts were lower after metal loading. The decrease was more pronounced in the catalysts prepared by impregnation (IMP-N and IMP-Cl) relative to the DP catalysts possibly due to occupation of the pores by larger Pd particles.

3.3. CO chemisorption studies

The results of CO chemisorption studies (Table 1), demonstrate that the IMP catalysts possessed low Pd dispersion compared to DP catalysts. The dispersion values for IMP-Cl, IMP-N were recorded as 6 and 4%, respectively whereas DP-N, DP-Cl catalysts recorded 11 and 22%, respectively. The lower dispersion values of IMP-N catalysts can be attributed to weak salt-support interaction, consequently large Pd particles were formed as the nitrate precursor decomposes easily at lower temperature. As the IMP-Cl catalyst was enriched with surface chloride species (Table 2), it was hard to eliminate the chloride

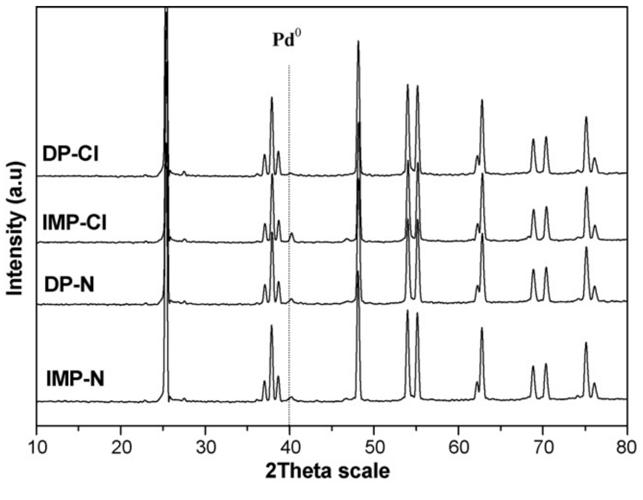

Fig. 2. XRD patterns of reduced TiO_2 supported Pd catalysts.

Table 1
Physico-chemical properties of TiO2 supported Pd catalysts

Catalyst	Surface area (m^2/gm)	CO uptake (μmol/gm)	Dispersion (%)	Specific metal surface area (m^2/gm)	Particle size (nm)	
					CO chemisorption	TEM
TiO_2	48	–	–	–	–	–
IMP-N	36	3.7	4	0.17	28.0	–
DP-N	42	10.3	11	0.49	10.2	12
IMP-Cl	38	5.6	6	0.26	18.6	–
DP-Cl	45	20.7	22	0.98	5.1	6.5

Table 2
Binding energy details and surface analysis data of Pd/TiO2 catalysts

Catalyst	Pd $3d_{5/2}$ binding energy (eV)	Peak intensity ratio of Pd $3d_{5/2}$/Ti $2P_{3/2}$	Cl/Pd*	
			Reduced	Spent
IMP-N	335.2	0.09	–	0.31
DP-N	335.3	0.28	–	0.22
IMP-Cl	337.4	0.12	0.28	0.51
DP-Cl	336.2	0.42	0.03	0.10

[*] Cl/Pd ratio determined by EDX analysis.

species from the catalyst surface even after calcination and reduction treatments. As a result, the CO adsorption capacity decreased. Interestingly, the DP-N catalyst exhibited relatively higher dispersion than IMP-N, which can be ascribed to difference in metal-support interaction.

In the case of DP-Cl catalyst, the $PdCl_2$ species precipitated as $Pd(OH)_2$, might have facilitated better metal-support interaction upon calcination showing higher dispersion value. It is known that chloride precursor of Pd offers better dispersion compared with the nitrate analogue particularly on supports bearing surface hydroxyl groups. It should also be borne in mind that the reduction temperature 300 °C was much lower than the conditions necessary for strong metal-support interaction (SMSI). Hence it is expected that the dispersion is usually higher.

3.4. Temperature programmed reduction

The TPR patterns of TiO_2 supported Pd catalysts are shown in Fig. 3. The profiles of IMP-Cl, IMP-N and DP-N catalysts exhibited a negative H_2 consumption peak in the range of 70–80 °C due to decomposition of β-PdH, which is a common feature of Pd catalysts associated with large particles [16,17]. The β-PdH might have been formed during the TPR experiment during the initial flushing of the catalyst with H_2/Ar mixture. An interesting observation that can be made here is that contrary to the other catalysts, DP-Cl exhibited a distinct positive H_2 consumption peak, characterized by the reduction of surface interacted PdO species. During DP method smaller Pd particles are formed as a result of salt-support interaction. The high dispersion value obtained by CO chemisorption on DP-Cl catalyst is a testimony for the presence of this positive peak.

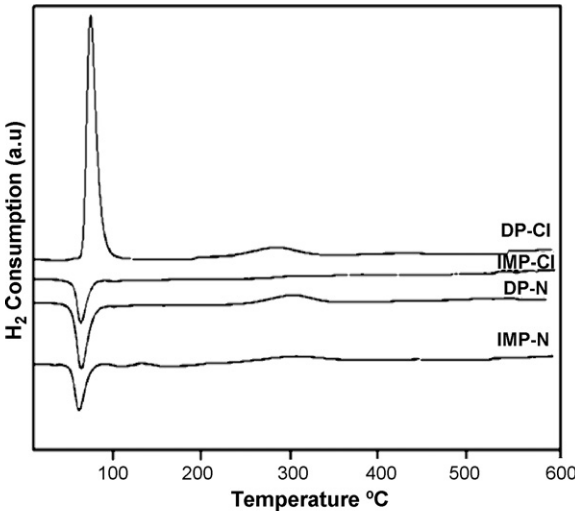

Fig. 3. TPR patterns of TiO_2 supported Pd catalysts.

The TPR characterization indicates that PdO particles originated from $PdCl_2$ were quite fine whereas those from $Pd(NO_3)_2$ were relatively larger as evidenced by the formation of Pd hydride. It can be further depicted that, in DP-Cl catalyst all the dispersed PdO particles were in close contact with titania but separated from each other, as evidenced by higher dispersion value. The dispersed phase where PdO interacts with titania cannot easily form large Pd particles. The H_2 consumption peak appearing at 300 °C in the case of DP-Cl catalyst may represent the reduction of TiO_2, because the presence of Pd^0 enhances the reduction of TiO_2. Shen et al. [23] also observed a decrease in TiO_2 reduction temperature in the presence of noble metals.

3.5. X-ray photoelectron spectroscopy (XPS)

The XPS results on the pre-reduced TiO_2 supported Pd catalysts are shown in Fig. 4. The Pd $3d_{5/2}$ B.E. value at 335.2 eV in IMP-N and DP-N catalysts can be attributed to the presence of metallic Pd

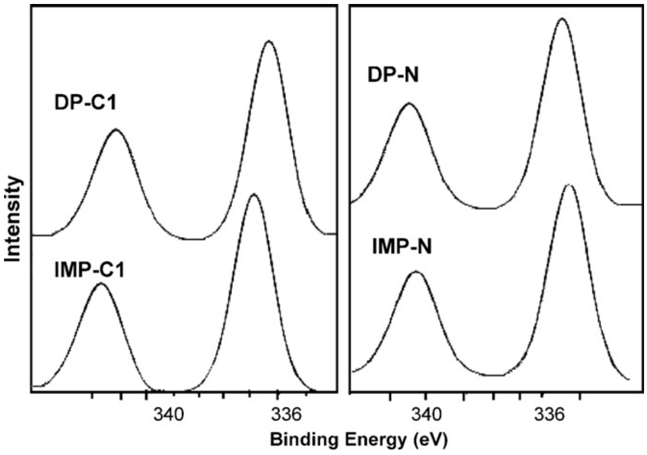

Fig. 4. XPS spectra of reduced TiO_2 supported Pd catalysts.

species as reported in the literature. It may be noted that irrespective of method of preparation, the catalysts prepared using $Pd(NO_3)_2$ precursor contained metallic Pd species. This can be explained as due to negligible salt-support interaction. However, the Pd $3d_{5/2}$ binding energy for IMP-Cl catalyst was recorded as 337.4 eV. This value corresponds to $PdCl_2$ moieties. As mentioned before it is very hard to eliminate the chloride species from the catalyst surface even after subjecting it to reduction treatment at 300 °C. An interesting observation that can be made is that, the reduced DP-Cl catalyst had Pd $3d_{5/2}$ B.E. equals to 336.2 eV, which was higher than the value shown for IMP-N and DP-N catalysts. The difference in the electronic state of Pd in DP-Cl could be due to difference in catalyst preparation and the nature of Pd precursor used. In the DP method, because of better salt-support interaction, electron transfer would be more facile from Pd to TiO_2 surface and consequently the electron deficient Pd (Pd^{n+}) species are generated. The surface analysis data obtained on the Pd/TiO_2 catalysts presented in Table 2 reveal that the peak intensity ratio of Pd $3d_{5/2}$ to Ti $2P_{3/2}$ was higher for DP-Cl catalyst than those obtained for IMP-N, IMP-Cl and DP-N catalysts. These values corroborated with those of dispersion obtained by CO chemisorption. Thus from XPS analysis it can be concluded that a facile formation of cationic Pd species is possible in DP-Cl catalyst.

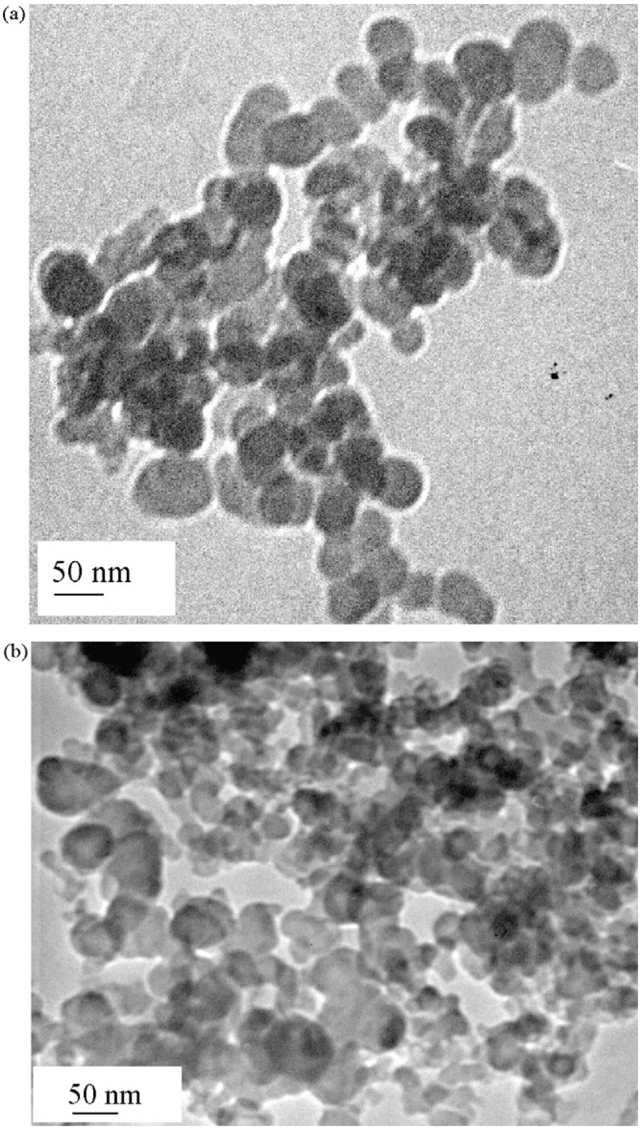

Fig. 5. TEM micrographs of reduced TiO_2 supported Pd catalysts (a) DP-Cl (b) DP-N.

3.6. Transmission electron microscopy (TEM)

The morphological features of reduced TiO_2 supported Pd catalysts were studied by transmission electron microscopy. The micrographs of DP-Cl and DP-N catalysts are shown in Fig. 5. They reveal that the DP-Cl catalyst possessed uniform distribution of Pd species on the TiO_2 support. The presence of flat Pd particles in DP-Cl catalyst can be attributed to formation of interacted Pd species with the TiO_2. The TEM image of DP-N catalyst exhibited large Pd particles with sperical shape and aggregated into large clusters. The discrepancy in morphology of Pd particle of the two catalysts can be attributed to change in the nature of Pd precursor and the extent of metal-support interaction. The particle size of Pd estimated by TEM measurement is comparable with the value obtained form CO chemisorption measurements (Table 1).

3.7. Activity measurements

The catalytic properties of TiO_2 supported Pd catalysts were evaluated for the gas phase hydrodechlorination of chlorobenzene operating at 140 °C and 1 atm pressure. The activity patterns of these catalysts are shown in Fig. 6. Benzene was obtained as a major product with negligible formation of cyclohexane. The activity profiles revealed that irrespective of metal precursor, the catalysts prepared from conventional impregnation method exhibited poorer activity. The continuous decline in catalytic activity of IMP catalysts can be attributed to weak salt-support interaction. During calcination palladium nitrate easily decomposes to PdO and aggregates into metallic Pd particles during reduction treatment, on which chlorine adsorption takes place as chlorine is an electrophilic molecule [12,24], thus leading to progressive deactivation.

The DP catalysts delivered higher specific HDC activity with better stability, irrespective of the metal precursor used. The variation of HDC conversion with reaction temperature is shown in Fig. 7. At any reaction temperature, the activity varied in the order DP-Cl > DP-N > IMP-Cl∼IMP-N. A linear increase in HDC activity was observed with increase in reaction temperature for all the catalysts. The exceptional HDC activity and stability of DP-Cl catalyst can be attributed the formation of Pd^{n+} species, which are formed due to strong interaction between titania and Pd. Literature also reveals that TiO_2 support facilitates better metal-support interaction [25–30]. However, the phenomenon of SMSI temperature of reduction was 300 °C only.

Our recent studies on Pd supported by rare earth oxides such as CeO_2, ZrO_2 have shown that catalysts prepared by the same

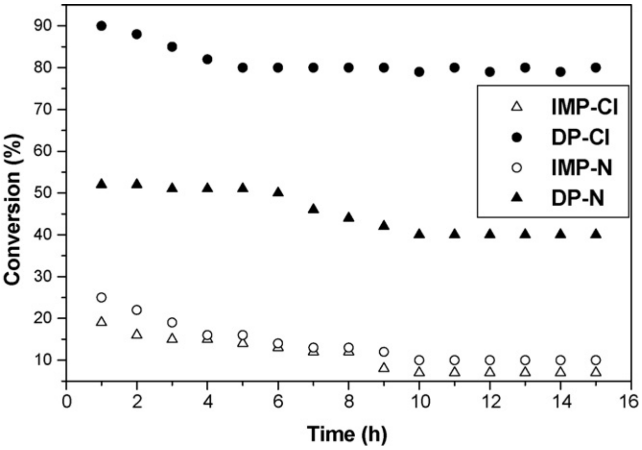

Fig. 6. Hydrodechlorination activity TiO_2 supported Pd catalysts.

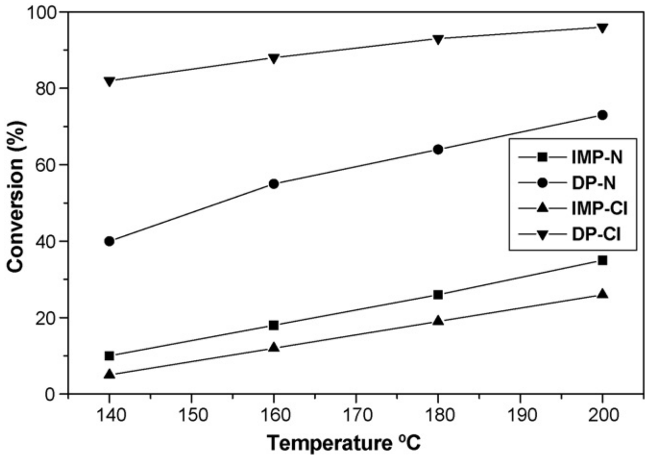

Fig. 7. Variation of HDC activity of TiO_2 supported Pd catalysts with reaction temperature.

deposition-precipitation method are highly active for hydrodechlorination of chlorobenzene [21,31]. The high catalytic activity of DP catalysts has also been reported for methanol decomposition and CO hydrogenation reactions [23,32–33]. The activity of catalysts depends on the extent of formation of cationic Pd species during the catalyst preparation. Among the various metal precursors, the chloride precursor of Pd interacts better than the nitrate precursor. The DP method of preparation helps formation of cationic Pd species. These species are found to be responsible for higher activity and stability.

In order to understand the reason for the difference in the stability, the spent Pd/TiO_2 catalysts were examined by EDX technique to quantify the surface chloride species formed during HDC reaction and the Cl/Pd ratios are shown in Table 2. The results demonstrate that, among all catalysts, IMP-Cl had higher chlorine content implying higher rate of deactivation. The DP-Cl on the other hand had lower chlorine content. The weak adsorption of chloride species [24] might be the reason for lower retention of chlorine on Pd^{n+} ion. Thus the Pd species is left active for the reaction.

4. Conclusions

Deposition-precipitation using chloride precursor of Pd is a better method for the preparation of Pd/TiO_2 catalysts used for hydrodechlorination reaction. Higher dispersion and a consequent formation of smaller Pd particles promoted electron transfer from Pd to TiO_2. The cationic Pd^{n+} ion thus formed is resistant to deactivation as the adsorption of chlorine on Pd^{n+} is weakened, and Pd remains active during the reaction.

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