

Studies on the modifications of Pd/Al₂O₃ and Pd/C systems to design highly active catalysts for hydrodechlorination of CFC-12 to HFC-32

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Abstract

The article highlights the various modifications of the support for Pd catalysts to enhance the hydrodechlorination ability to synthesize dichlorodifluoromethane (HFC-32). The supports studied for the modification are either alumina (Al₂O₃) or carbon. In the modification of oxidic support, especially Al₂O₃, the main objective is to prevent to the maximum extent the transformation of oxidic support to the corresponding oxy/hydroxy fluorides due to the release of HF during the course of hydrodehalogenation reaction. Modification of Al₂O₃ support has been achieved by covering with carbon, called carbon-covered alumina (CCA), and simultaneous coverage with carbon and fluorine, called fluorinated carbon-covered alumina (FCCA). In the case of carbon as support, even though Pd/C exhibits good conversion in the hydrodehalogenation of CCl₂F₂, the selectivity towards HFC-32 is poor, and hence the modification of carbon support is aimed to enhance the selectivity towards HFC-32. Modification of carbon support has been achieved by incorporation of either MgO, ZrO₂, or Al₂O₃. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrodehalogenation; Pd catalysts; Modification of support; HFC-32

1. Introduction

In recent times, the environmentalists all over the world have become extremely critical about the environmental problems, particularly the ozone depletion problem posed largely by chlorofluorocarbons (CFCs) [1–6]. The world is moving rapidly towards the phase out of CFCs. In spite of the prohibition on the production and use of CFCs, the depletion of stratospheric ozone still continues because of the presence of existing stocks of CFCs and other ozone-depleting substances. Even though several destruction methods [7–13] are listed in literature, these methods are energy-intensive processes and yield HF, HCl, CO, COCl₂ and CO₂ that will again increase the global warming. Hence, converting CFCs into value-added substances is a logical step. Among the conversion processes, selective hydrodechlorination of CFCs has been identified as a better process for their transformation as it yields either

hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) that have low or almost zero ozone depletion potential (ODP) value [14–18]. Selective hydrodechlorination of CCl₂F₂ (CFC-12) yields CH₂F₂ (HFC-32) which has zero ODP value with properties close to a substance used as a deep refrigerant [17,18].

Majority of the hydrodechlorination studies in the literature are cited with Pd supported on either Al₂O₃ or C as support. Both supports have their own merits and demerits. The advantages of alumina (Al₂O₃) as support are its interactive nature with most of the active components and its mechanical strength. The major disadvantage with this support is its susceptibility towards HF or HCl released during hydrodehalogenation of CFCs. On the other hand, activated carbon being a high-surface area support, the main advantage is to keep Pd in highly dispersed state. However, smaller particles of Pd are highly active and hence not only dechlorination but also defluorination can take place; therefore, the selectivity towards dechlorination product decreases. The present review highlights some of the ways to overcome the difficulties encountered with Al₂O₃ and C as supports.

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2. Results and discussion

Coq et al. [19] have proposed a reaction mechanism for hydrodehalogenation of CFC-12 over Pd surface. According to their mechanism, the formation of CH_2F_2 depends on the formation of surface intermediate CF_2^* species followed by its rate of desorption of these species. If the residence time of this species on Pd surface is more, then further dehalogenation occurs and the reaction ends with the formation of CH_4 . Thus, in order to halt the reaction at CH_2F_2 , it is necessary to make Pd more electron deficient, which results in the easy desorption of this surface intermediate. Juszczuk et al. [20], in their work on Pd/ Al_2O_3 catalysts, have observed that poorly dispersed Pd catalysts are active and selective in the CCl_2F_2 hydrogenolysis. Studies by Coq et al. [14,19,21] reveal that chlorination/dechlorination of the metallic surface of the catalyst is the key step in controlling the reaction rate. They have also observed that smaller particles of Pd decrease the selectivity of CH_2F_2 . They have explained the positive role of AlF_x layer at the periphery of the Pd particle, which withdraws the F atoms and protects the Pd particles against diffusion of F into the bulk. Juszczuk et al. [20] have studied that larger particles of Pd get easily transformed into palladium carbide and are more active towards hydrogenolysis of CFC-12 and selective towards CH_2F_2 . They are of the opinion that the bulky Pd particles constitute a more capacious sink for carbon than smaller Pd particles in highly dispersed catalysts. Larger Pd crystallite contains higher proportions of surface plane sites, which bind the C_1 species more strongly than the corners and edges of the unsaturated sites. The studies by Bell et al. [22] on the conversion of CCl_2F_2 on $\gamma\text{-Al}_2\text{O}_3$ revealed that chlorination and fluorination of Al_2O_3 produces an active catalyst surface.

Pd/ Al_2O_3 and Pd/C are widely employed for the hydrodehalogenation of CFC-12. Both the catalysts have several advantages and disadvantages. In order to get HFC-32 selectively, there are two ways. One is the modification of Al_2O_3 support and the other one is the modification of carbon support. In the following sections, various ways of modification of these supports to achieve high conversion of CFC-12 and high selectivity towards HFC-32 in the hydrodehalogenation reaction are discussed.

2.1. Modification of Al_2O_3 support

Several studies have been focused on the role of support [14,19,23–27], the influence/nature of a second metal as a promoter [15,19,21,28] and the reaction pathways [15]. Pd, supported on the oxide supports particularly Al_2O_3 and TiO_2 , showed changes in the selectivity as a function of time on stream and this is ascribed to the reaction of the oxide support with HF released during the reaction.

2.2. Modification of Al_2O_3 support by carbon coverage and simultaneous coverage with fluorine and carbon

Carbon-covered alumina (CCA) has been reported to be a better support for promoted Ru catalyst for low-temperature ammonia synthesis at atmospheric pressure [29]. Carbon-covered alumina possesses the beneficial properties of both alumina and carbon, like good mechanical strength (due to the presence of alumina) and reduction in metal–support interaction (due to the presence of carbon that covers the alumina). In view of the beneficial role of carbon coverage on alumina, we have investigated Pd-supported CCA as a catalyst for selective hydrogenolysis of CFC-12 to HFC-32 [30]. The CCA support employed in this study has been prepared by taking γ -alumina in a quartz reactor and passing nitrogen saturated with cyclohexene vapour for 10 h at 600°C adopting the procedure described by Boorman et al. [31]. From the TPR experiments, it is observed that carbon present in CCA is of two different types: the first one being reduced in low-temperature region is of either free carbon or a carbon with low H_2 content, and the second one being reduced in high-temperature region is due to hydrogen-rich carbon (CH_x where $x > 2$). TPR experiments conducted on active carbon reveal that the reduction of carbon occurs in two stages: a low-temperature one; and a high-temperature one. But both these species may be attributed to the gasification of similar carbonaceous species of active carbon. These carbonaceous species are originated due to either free carbon or hydrocarbon moiety with lower hydrogen concentration (CH_x , where $x < 2$). Activated carbon is a high-surface area material, whereas the carbon in CCA contributed to the surface area reduction of alumina. Even though the carbon covered on alumina has been generated by pyrolysis process, from the TPR results one can assume that the strong acid centers of Al_2O_3 might have been covered with H_2 -rich CH_x moiety and the moderate sites might have been covered with free carbon or CH_x with lower H_2 .

In Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalysts, transformation of Al_2O_3 , during the initial hours of CCl_2F_2 hydrogenolysis reaction, into aluminum oxy/hydroxy fluorides has a beneficial effect in getting high CH_2F_2 selectivity after attaining steady state [19–21,32], but the same is responsible for activity loss. In order to improve the stability of the catalyst during reaction, particularly in minimizing the transformation of Al_2O_3 into its oxy/hydroxy fluorides, an attempt has been made for the first time to find out the effect of fluorinated carbon-covered alumina (FCCA) as a support in Pd/FCCA catalyst in the hydrodehalogenation of CCl_2F_2 [33]. The FCCA support has been prepared by pyrolysis of fluorobenzene on $\gamma\text{-Al}_2\text{O}_3$ by the method reported by Boorman et al. [31]. TPR results of FCCA indicate the nature of carbon in FCCA is similar to the one present in CCA.

The steady-state activity over Pd/ $\gamma\text{-Al}_2\text{O}_3$, Pd/C, Pd/CCA and Pd/FCCA catalysts against reaction temperature [33]

reveals that loss of conversion against temperature is very high over Pd/Al₂O₃ and, to a lower extent, over Pd/CCA particularly beyond 240 °C. The activity loss is due to the transformation of Al₂O₃ into Al-oxo/hydroxy fluorides. Even though over Pd/C the conversion is high (100% at 260 °C), most of the CCl₂F₂ is converted to CH₄ with comparatively low selectivity towards CH₂F₂. The high conversions of CCl₂F₂ mostly into CH₄ over Pd/C may be due to high dispersion of Pd on carbon. Occlusion of fluorine into Pd in Pd/C or Pd/graphite has been reported as the reason for the low selectivity towards CH₂F₂ [21]. The high selectivity towards CH₂F₂ over Pd/FCCA and negligible decrease in activity with increase in reaction temperature are the advantages of FCCA support. The carbon coverage in minimizing the interaction between Pd and Al₂O₃ and the presence of Al-fluoride in FCCA, which results in increasing the partial dehalogenation ability of Pd required for the selective removal of chlorine from the CCl₂F₂ molecule, are responsible factors for the high selectivity towards CH₂F₂. Coq et al. [19] and Shekar et al. [30] studied the hydrodechlorination of CCl₂F₂ over Pd/AlF₃ and explained the role of fluoride moiety in partial electron transfer from Pd to the carrier due to the presence of fluorine atoms at the metal–support interface. In Pd/Al₂O₃, as the conversion of Al₂O₃ into oxo or hydroxo fluorides proceeds, there is every possibility of Pd metal particles burial in the AlF₃ or Al-oxo/hydroxo fluorides making them inaccessible for exposure to CCl₂F₂ and hence low activity. Even though in Pd/CCA the interaction between Pd and Al₂O₃ (in support) is lower than that of Pd/Al₂O₃ catalysts, the transformation of Al₂O₃ into Al-oxo/hydroxo fluorides may still be possible, which is evidenced from the XRD results of used catalysts. The catalyst Pd/FCCA initially contains α-AlF₃ species, which are formed during the preparation stage of FCCA itself, and hence there is no question of Pd burial in AlF₃ during the course of reaction. Even after 40 h the Pd/FCCA shows stable activity and selectivity (~50% CH₂F₂ yields) at a reaction temperature of 240 °C. Below 240 °C where support transformation is not possible, Pd/CCA exhibited very good activity. Minimized metal support interaction between Pd/γ-Al₂O₃ in CCA may be helping in preventing the Pd-lattice burial upon hydrogenolysis reaction of CFC-12, helping in getting higher HFC-32 selectivity.

2.3. Modification of carbon support

The advantage of Pd/C catalysts is its high conversion because of higher dispersion of Pd and this higher dispersion of Pd however, leads to deep hydrogenated product i.e., CH₄. In order to eliminate the disadvantage associated with carbon support, an attempt has been made to find out the promotional effect of certain inorganic oxides in Pd/C catalysts.

It may be noted that ZrO₂ is resistant to HF or HCl liberated during the hydrogenolysis of CCl₂F₂ over Pd/ZrO₂ compared to Pd/Al₂O₃ and Pd/TiO₂ catalysts [19]. In order

to find out the combined effect of ZrO₂ and C, a catalyst containing 4 wt.% Pd and 10 wt.% ZrO₂ on carbon, prepared by co-impregnation method, has been studied for the hydrodechlorination of CFC-12 [34]. Similarly, it was reported that deposition of higher amounts of F⁻ on the surface of Pd/MgO than on Pd/Al₂O₃ is helpful in yielding better activity on the former [18]. This prompted the authors to find out the synergistic effect of MgO and C in Pd-MgO/C catalyst for the hydrodechlorination of CFC-12. There are only few reports available for the hydrodechlorination of CFCs over Pd supported on basic catalysts [27,35–37]. The reason may be the low resistance expected to be offered by these catalysts towards the corrosive reaction conditions during the course of reaction. But, the reports on hydrodechlorination of carbon tetrachloride (CCl₄) over Pt/MgO [38] and hydrodechlorination of CCl₂F₂ over Pd/MgF₂ [36] have indicated that these catalysts are highly stable during the reaction conditions. In our earlier studies [17,18], we have found stable activity and high selectivity towards CH₂F₂ in the hydrodechlorination of CCl₂F₂ over Pd supported on hydrotalcite precursors and Pd/MgO catalysts. Pd-MgO/C catalyst was prepared by co-impregnation of activated carbon support with acidified aqueous solution containing requisite amounts of PdCl₂ and Mg(NO₃)₂ to give a Pd loading of 4 wt.% and a Mg content of 10 wt.% as MgO [39].

The CO-chemisorption and BET surface area values of Pd-ZrO₂/C and Pd-MgO/C catalysts [34,39], respectively, indicate the formation of bigger crystallites of Pd compared to that in Pd/C catalyst. However, the BET surface areas of Pd-ZrO₂/C and Pd-MgO/C catalysts compared to that of Pd/C catalyst are higher, indicating that the extra area might have generated from the smaller particles of ZrO₂ and MgO, respectively. XRD data indicate the presence of monoclinic ZrO₂ in Pd/ZrO₂ fresh, reduced and spent catalysts, whereas in Pd-ZrO₂/C fresh catalyst, ZrO₂ is amorphous. This may be because of the lower content of ZrO₂. However, in the used Pd-ZrO₂/C catalyst, signals due to Zr fluoride have been found. This clearly indicates that ZrO₂ in Pd-ZrO₂/C is susceptible to HF released during the reaction whereas the monoclinic ZrO₂ phase in Pd/ZrO₂ catalyst is resistant to HF or HCl released during the reaction. The amounts of F⁻ in the Pd/C, Pd/ZrO₂ and Pd-ZrO₂/C spent catalysts (1.78, 1.81 and 7.04 wt.%, respectively) clearly indicate fluorination of ZrO₂ phase in Pd-ZrO₂/C catalyst. Thus, in order to make ZrO₂ susceptible to HF, it is essential to have amorphous ZrO₂ phase in the catalyst. In addition to ZrF₄ phase in Pd-Zr/C spent catalyst, signals due to PdC_x were also observed. The formation of PdC_x phase can be explained as follows. Juszczyk et al. [20] have observed the formation of PdC_x from Pd during the hydrodechlorination of CCl₂F₂ over Pd supported on γ-Al₂O₃ catalysts. Sandt et al. [40] have also observed the presence of PdC_x phase in the spent catalysts used for the hydrodechlorination of CCl₂F₂ over palladium black catalyst. In a study [41] Pd supported on ZrO₂ showed a better resistance to chlorine than on the other supports used, viz., SiO₂/AlPO₄

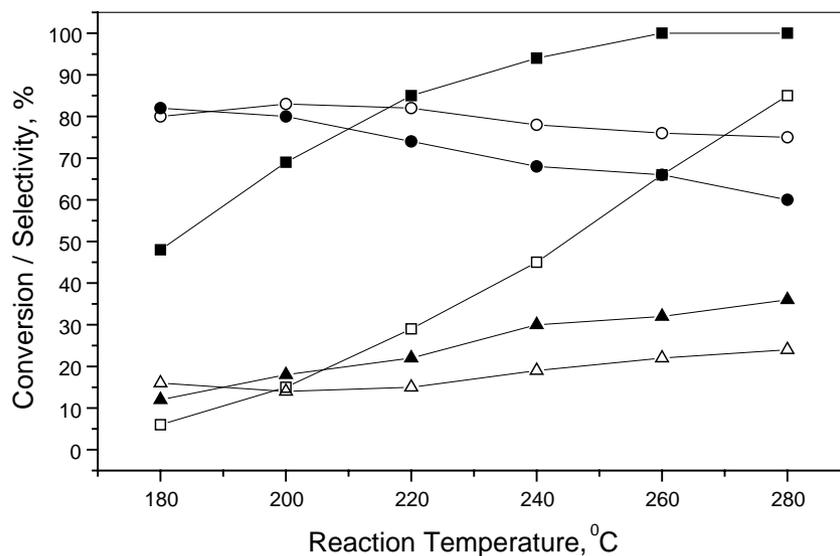


Fig. 1. Effect of reaction temperature in the hydrodechlorination of CCl_2F_2 over Pd-ZrO₂/C and Pd-MgO/C catalysts at a GHSV = 4800 h⁻¹ and $\text{H}_2/\text{CCl}_2\text{F}_2 = 8$. Pd-ZrO₂/C: ■ = conversion of CCl_2F_2 ; ● = selectivity of CH_2F_2 ; ▲ = selectivity of CH_4 . Pd-MgO/C: □ = Conversion of CCl_2F_2 ; ○ = selectivity of CH_2F_2 ; △ = selectivity of CH_4 .

and MgO, in the liquid phase hydrodechlorination of chlorobenzene.

The steady-state product composition over Pd-ZrO₂/C and Pd-MgO/C catalysts at different reaction temperatures are shown in Fig. 1. It is remarkable to note that at 180 °C the conversion of CCl_2F_2 and selectivity to CH_2F_2 are almost double on Pd-Zr/C compared to those on Pd/C [34]. At 280 °C, while both the catalysts showed 100% conversion, the selectivity to CH_2F_2 on Pd-Zr/C (60%) is almost three times that of Pd/C (22%) [34]. The conversion and selectivity to CH_2F_2 on Pd/ZrO₂ is poor at all the reaction temperatures. As a whole, the activity studies indicate the selective formation of CHClF_2 on Pd/ZrO₂, CH_4 on Pd/C, and CH_2F_2 on Pd-Zr/C, respectively [34]. The higher dispersion (smaller particle size) of Pd in Pd/C leads to the formation of CH_4 . In Pd/ZrO₂ catalyst-associative desorption of surface intermediate CF_2^* species with adsorbed Cl species leads to the formation of CHClF_2 [42]. Selectivities to CHClF_2 and CH_4 are comparatively lower on this catalyst. In the case of Pd-MgO/C catalyst (Fig. 1), the main products observed are CH_2F_2 and CH_4 along with the formation of the other products like CHClF_2 and CH_3F , and at higher temperatures above 250 °C, the formation of other by-products like CHCl_2F and trace amounts of Cl/F exchange-type products are also observed. Conversion of CCl_2F_2 increased from around 5% to >85% with increase in reaction temperature from 180 to 280 °C on Pd-MgO/C. The selectivity to CH_2F_2 is more or less constant till 260 °C and beyond this slightly decreased, and a corresponding increase in selectivity to CH_4 is observed with the increase in reaction temperature. However, 260 °C seems to be the optimum reaction temperature as the selectivity towards CH_2F_2 is found to be reasonably good at this reaction temperature. In conclusion, higher selectivity to CH_2F_2 over zirconium ion-modified Pd/C and

MgO-modified Pd/C catalysts is thought to be associated with the Lewis acidity of fluorinated species generated during the reaction. These metal fluoride species are responsible for the electron-deficient Pd sites, which may favour the easy hydrogenative desorption of CF_2^* species to produce CH_2F_2 .

The higher selectivity to CH_2F_2 over Pd/MgO or Pd/MgF₂ catalysts may be explained on the basis of the mechanism proposed by Coq et al. [14] that the Lewis acidity of the MgF_2 support similar to that over AlF_3 makes Pd more electron deficient, thus, enhancing the selectivity towards CH_2F_2 through easier desorption of the CF_2^* species. The lower electron density of the Pd favors the desorption of CF_2^* , the most abundant surface intermediate, and hence the selectivity to CH_2F_2 . The presence of F^- in Pd-MgO/C or in Pd-ZrO₂/C make Pd more electron deficient. The co-impregnation of Pd and MgO over C or Pd and ZrO₂ over C has facilitated a better interaction between Pd and Mg or Pd and Zr species, respectively, giving much higher selectivity to CH_2F_2 . The synergistic effect between Pd/MgO and Pd/C and Pd/ZrO₂ and Pd/C seems to be the main reason for the high activity over these catalysts.

It has been reported that Pd/ AlF_3 is more selective in yielding HFC-32, and Pd/graphite is more selective for CH_4 formation in the hydrogenolysis of CFC-12 [19]. Even though Pd/CCA catalyst exhibited good selectivity towards HFC-32, the conversion of CFC-12 is not high as that on activated carbon. Hence, an attempt has been made to modify the characteristics of Pd/C catalyst by incorporation of small amount of aluminum-precursor, preferably as isopropoxide to improve the selectivity towards HFC-32 without compromising with the conversion of CCl_2F_2 on Pd/C catalysts [43]. By selecting aluminum isopropoxide, an organic-precursor, to deposit on activated carbon, it is

possible to obtain highly dispersed aluminum oxide/fluoride species on carbon. Co-impregnation of Pd and Al precursors on activated carbon is to maintain the interaction between Pd and aluminum species and the resultant catalyst is termed as PAC. This catalyst is expected to yield combined characteristics of Pd/C and Pd/Al₂O₃.

The CO uptake is found to be high in Pd/C catalyst (32 $\mu\text{mol/g}$) than in PAC catalyst (8.2 $\mu\text{mol/g}$). Due to high dispersion of Pd on carbon support, crystallite size of Pd is low (14 nm), whereas in the PAC catalyst the Pd dispersion is low, resulting in the formation of bigger particles of Pd (54 nm). It is interesting to note that even though the Pd dispersion is quite higher on Pd/C catalyst (8.5%) when compared to PAC (2.2%), its total surface area (586 m^2/g) is lower than the PAC catalyst (681 m^2/g). This is an indication of strong interaction between Pd- and Al-precursor and the extra area is due to the smaller Al-precursor particles generated upon reduction. XRD pattern (Fig. 2) of PC/C-reduced catalyst does not show any signals due to Pd, due to its high dispersion, which indicates the presence of Pd in small crystallites. Whereas in PAC-reduced catalyst, signals due to α -Pd are observed, indicating the formation of bigger Pd particles and stabilization of Pd on aluminum oxide species instead of diffusion into carbon pores. It is interesting to observe that in the PAC-used catalyst, XRD signals due to α -AlF₃ are observed, which are formed during the course of CFC-12 hydrogenolysis reaction, by the interaction of Al-precursor with HF.

Coq et al. [19] studied and reported high selectivity towards CH₂F₂ using Pd/AlF₃ catalysts compared to other catalysts. During the course of CCl₂F₂ hydrogenation, these α -AlF₃ species would withdraw adsorbed fluorine atoms, thereby scavenging the surface which helps to protect the Pd particles against diffusion of fluorine into the bulk. The same authors reported that under the corrosive reaction con-

ditions where HF and HCl are formed as by-products, transformation of alumina into AlF_{1.65}(OH)_{1.35}·*x*H₂O species. Kanta Rao and co-workers [44] reported the transformation of catalyst material into metal-oxy/hydroxy fluorides during the dismutation of CCl₂F₂ over alumina-based catalysts, and Kemnitz and co-workers [45] reported the formation of large amount of AlF₂(OH) pyrochlore structure during the activation of γ -Al₂O₃ with CFC molecule in gas phase. However, in the PAC-used catalyst, signals due to α -AlF₃, which plays major role in obtaining the high selectivity towards desired product CH₂F₂ have been observed. This clearly indicated the advantage of incorporation of aluminum salt along with PdCl₂ to the carbon support. XRD signals due to PdC_{*x*} are observed in the used Pd/C catalyst. Sandt et al. [40,46] substantiated the PdC_{*x*} formation during the hydrodechlorination of CCl₂F₂ over 2 and 3 wt.% Pd/C and Pd black catalysts.

In this investigation, the major products observed over PAC catalyst are CH₂F₂ and CH₄ along with small amounts of CHClF₂. The HF formed in the reaction is responsible to yield Al-fluorides. Time on stream analysis of hydrodechlorination of CFC-12 at a reaction temperature of 180 °C on Pd/C and PAC catalysts reveal that on PAC catalyst, initially a very low conversion and high selectivity to CH₄ is observed, which indicates that during the first 60-min time on stream, both dechlorination and defluorination occurred leading to the formation of methane, and the HF released in this process attack some part of aluminum-precursor present on the surface to get α -AlF₃ species (evidenced from XRD). After a period of 60 min, steady-state conversion of CFC-12 with high selectivity towards HFC-32 has been attained. In the Pd/C catalyst, both conversion of CCl₂F₂ and selectivity to CH₂F₂ decreases during the unsteady-state period. This clearly indicates the advantageous role of α -AlF₃ formed in the PAC catalyst during the course of CFC-12

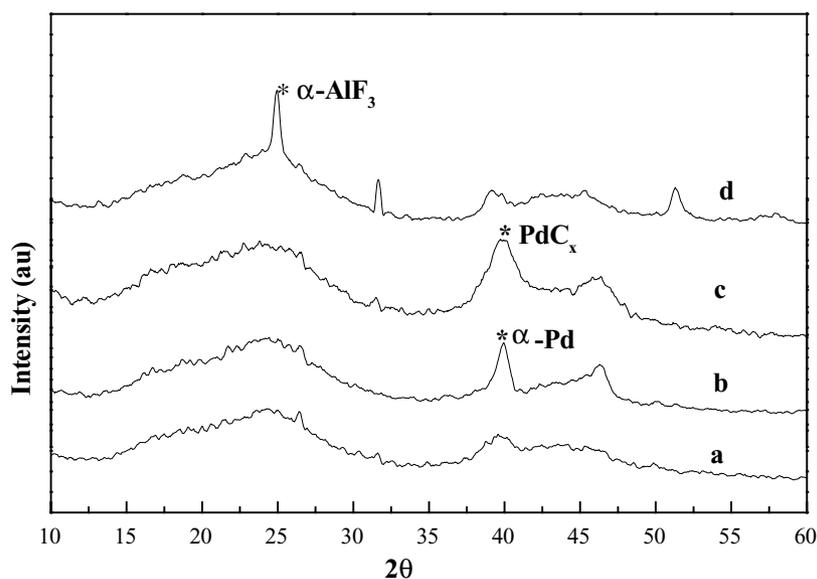


Fig. 2. XRD patterns of catalysts: (a) PC-reduced; (b) PAC-reduced; (c) PC-used; and (d) PAC-used.

hydrogenolysis reaction. Fluoride content is also observed in more quantities in PAC-used catalyst (2.55 wt.%) than in PC-used catalyst (1.78 wt.%). Steady-state activity results in the hydrodechlorination of CCl_2F_2 as a function of reaction temperature over PC and PAC catalysts indicate that at a reaction temperature of 180°C , the CFC-12 conversions and selectivities towards HFC-32 are 9% and 46% over Pd/C and 30% and 96% over PAC catalysts, respectively. The conversion of CCl_2F_2 on both PC and PAC catalysts are almost same (47% and 44%, respectively), at 200°C but selectivity to CH_2F_2 on PAC (91%) is double than that on PC (45%) and increased on PAC with nearly three times than that on PC at 260°C (selectivity to CH_2F_2 is 26% and 86% on PC and PAC catalysts, respectively). PAC catalyst has been continuously tested for the hydrodechlorination of CCl_2F_2 at 250°C with a gas hourly space velocity of 4800 h^{-1} and $\text{H}_2/\text{CFC-12} = 8$. This catalyst exhibited $\sim 82\%$ conversion of CCl_2F_2 with 88% selectivity towards CH_2F_2 in 12 h time on stream which indicates that the catalyst has not suffered any loss of activity. It may be concluded that the synergetic interaction between Pd and Al and the Lewis acidity of AlF_3 , which is formed during the reaction makes Pd more electron deficient, thus enhancing the selectivity towards CH_2F_2 through easier desorption of the surface intermediate $^*\text{CF}_2$ species. Thus, the characteristics of new aluminum isopropoxide-modified carbon-supported Pd catalyst are useful in designing a commercial catalyst for selective hydrodechlorination of CCl_2F_2 to produce ozone-friendly compound CH_2F_2 .

In the hydrodehalogenation of CCl_2F_2 , not only the particle size of Pd but also other factors like the environment of Pd and the interaction of second metal with Pd are important factors in controlling the deep halogenation and yielding HFC-32 more selectively.

3. Conclusions

From this review the following conclusions are drawn:

1. Modification of Al_2O_3 support by carbon coverage or by carbon and fluorine incorporation simultaneously has been beneficial in designing a good Pd-based catalysts for hydrodechlorination of CFC-12 to selectively get HFC-32. The combined characteristics of Pd/ Al_2O_3 and Pd/C in PdCCA and, additionally, the presence of F^- ion in PdFCCA are mainly responsible for getting high activity over these catalysts compared to Pd/C and Pd/ Al_2O_3 .
2. The nature of carbon in Pd/CCA and Pd/FCCA are similar but is different from the nature of carbon present in activated carbon. In activated carbon, the carbon with less hydrogen content may be free carbon or a CH_x moiety with $x < 2$ which is getting reduced in two stages. In CCA and FCCA, the nature of carbon which gets reduced at lower temperature is similar to the one present in activated carbon, and the carbon which gets reduced at high temperature region is a hydrogen-rich CH_x moiety where $x > 2$.
3. Modification of carbon by either by ZrO_2 addition or by MgO incorporation is advantageous because the ZrO_2 in Pd- ZrO_2/C and MgO in Pd-MgO/C are susceptible to HF released during the hydrogenolysis forming ZrF_4 and MgF_2 phases respectively, which responsible for creating electron-deficient environment at the vicinity of Pd site. It is thus helpful to selectively yield HFC-32.
4. Modification of carbon by adding Al-isopropoxide-precursor resulted in a good Pd-Al/C catalyst for the selective synthesis of HFC-32 in the hydrodechlorination of CFC-12. The Al_2O_3 present in this catalyst is susceptible to HF and is helpful for getting high conversion and selectivity.
5. The above conclusions are helpful in designing a highly active and stable hydrodechlorination catalyst for the synthesis of HFC-32 at atmospheric pressure.

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