

# Selective hydrogenolysis of dichlorodifluoromethane on carbon covered alumina supported palladium catalyst

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## Abstract

$\gamma$ -Alumina is modified by carbon coverage and the resulting carbon covered alumina is used in the preparation of supported Pd catalysts with varying Pd loadings. The prepared catalysts have been characterized by BET surface area, CO-chemisorption, X-ray diffraction and temperature programmed reduction (TPR). The catalytic activities of these catalysts have been tested for the selective hydrogenolysis of dichlorodifluoromethane to difluoromethane. TPR studies reveal that fresh Pd/CCA catalysts at lower Pd loading (up to 4 wt.%) exhibit features of Pd/Al<sub>2</sub>O<sub>3</sub> (decomposition of  $\beta$ -PdH<sub>x</sub>) along with Pd/C (reaction of Cl<sup>-</sup> with hydrogen) and beyond 4 wt.%, only Pd/C features are observed. TPR of spent catalysts reveal the increase in the intensity of  $\beta$ -PdH<sub>x</sub> with increase in Pd loading indicating the reorganization of Pd particles during the course of hydrogenolysis reaction. TPR of CCA and active carbon supports showed that the nature of carbon is somewhat different in CCA and active carbon. XRD data has shown that some amount of uncovered alumina is converted into its hydroxide fluoride. High selectivity to HFC-32 (~95%) over 4 wt.% Pd/CCA catalyst at a reaction temperature of 220 °C is attributed to the beneficial role of carbon coverage on  $\gamma$ -alumina.

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**Keywords:** Hydrogenolysis; TPR; Dichlorodifluoromethane; Carbon covered alumina

## 1. Introduction

Dichlorodifluoromethane (CCl<sub>2</sub>F<sub>2</sub>) is a large tonnage chlorofluorocarbon (CFC) used extensively in refrigeration and air-conditioning. CFCs have been identified as chief components in depleting the stratospheric ozone, creating holes in the layer [1]. There has been worldwide ban on the production and usage of CFCs, stipulating cut-off dates. However, the existing stocks need to be disposed off safely. Selective hydrogenolysis of CFCs over suitable catalysts yields

hydrofluorocarbons (HFCs) with zero ozone depleting potential (ODP) and they are also useful as CFC alternatives [2,3]. Palladium-based catalysts have been widely studied for selective hydrogenolysis of CFCs to obtain useful products. Conversion of CCl<sub>2</sub>F<sub>2</sub> (CFC-12) over a catalyst under hydrogen yields CH<sub>2</sub>F<sub>2</sub> (HFC-32), an ozone benign substance useful as a deep refrigerant. Several studies have been focused on the role of support [4–10], palladium black as a model catalyst [11], the influence of a second metal as a promoter [6,12–14], the reaction kinetics [5,6,9] and reaction pathways [14]. Microwave heating [15] and high temperature reduction [16] have been used to obtain poorly dispersed supported Pd catalysts. Recently, the characteristics and activity of poorly dispersed Pd catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and active carbon are

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compared [17]. Choosing a right support is important in getting high catalytic activity and selectivity towards HFC-32. It has been reported that while Pd/AlF<sub>3</sub> is more selective in yielding HFC-32, Pd/graphite is more selective for CH<sub>4</sub> formation in the hydrogenolysis of CFC-12 [5]. Carbon covered alumina (CCA) has been reported to be a superior support for promoted Ru catalyst for low temperature ammonia synthesis at atmospheric pressure [18]. CCA possesses the beneficial properties of both alumina and carbon, like good mechanical strength (due to the presence of alumina), 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. The results on the effect of Pd loading, H<sub>2</sub>/CFC-12 ratio, reaction temperature and GHSV on the conversion of CFC-12 and selectivity to HFC-32 and CH<sub>4</sub> are reported in this communication. The catalyst characteristics carried out by XRD, CO-chemisorption, and TPR are correlated with catalytic activities wherever possible.

## 2. Experimental

Commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Harshaw, BET SA: 260 m<sup>2</sup> g<sup>-1</sup>) is crushed and sieved to 18/25 BSS and then calcined at 400 °C for 3 h. The CCA support is prepared by taking this alumina in a quartz reactor and passing nitrogen saturated with cyclohexene vapor for 10 h at 600 °C adopting the procedure described by Boorman et al. [19]. The carbon content in CCA thus prepared is found to be 24 wt.% determined by gravimetric analysis. The CCA supported palladium catalysts are prepared by wet impregnation of the CCA with requisite amount of acidified (with HCl) aqueous solution (0.134 g Pd/ml) of PdCl<sub>2</sub> (PdCl<sub>2</sub>, Aldrich, USA). The excess solution is evaporated on a water bath till dryness and then further dried in an oven at 100 °C for 12 h. A portion of each of the oven dried catalyst sample is reduced in hydrogen at 400 °C for 4 h and then passivated in N<sub>2</sub> atmosphere. The reduced samples are used for XRD studies. Palladium loading on CCA is varied from 2 to 10 wt.% and the catalysts are designated as PCCA1, PCCA2, PCCA3, PCCA4 and PCCA5, which contain 2, 4, 6, 8 and 10 wt.% of Pd, respectively. The carbon content

in reduced PCCA2 is found to be 20 wt.%. The decrease in carbon content in reduced catalyst compared to that of the pure support may be attributed to: (i) contribution of Pd in the catalyst and (ii) gasification of carbon during reduction.

XRD analysis of fresh, reduced and used catalysts is carried out on a Siemens D5000 X-ray diffractometer using Cu K $\alpha$  radiation.

CO-chemisorption capacities of the catalysts are determined at room temperature on an all glass high vacuum unit using double isotherm method assuming a chemisorption stoichiometry of 1:1 between CO and Pd [20]. The dispersion, metal surface area (MSA) and Pd particle size (PS) in catalyst are calculated according to the procedure described by Scholten et al. [21]. Experimental details and procedures are as described by Mahata and Vishwanathan [20]. Prior to CO-chemisorption experiments, the catalyst is reduced in the H<sub>2</sub> flow (40 ml/min) at 400 °C for 4 h. BET surface areas of the reduced catalysts were determined by N<sub>2</sub> adsorption at –196 °C.

A lab made equipment fabricated by us is used to carry out TPR experiments. A microprocessor controlled sensitive conductivity meter (sensitivity 0.1  $\mu$ S; cell constant = 0.98; M/s Systronics, India) is used to determine the conductivity of a KOH solution (0.005 M) kept between the outlet of the reactor and TCD/FID-gas chromatograph (GC). The KOH solution neutralizes the HCl/HF formed during reduction of the catalyst. The details of this setup and experimental procedure adopted are described elsewhere [22]. In all the TPR experiments the catalyst (100–150 mg) bed temperature is programmed at a rate of heating of 11 °C/min from room temperature to 700 °C and then kept isothermal at that temperature for 30 min. A 6% H<sub>2</sub> in Ar is used as reducing gas. Prior to the start of the temperature program, the reducing gas mixture is passed (20 ml/min) over the catalyst for about 30 min. It may be noted that dried catalyst samples are used for TPR experiment. In order to understand the nature of carbon in the CCA support two TPR runs are carried out. TPR-I patterns correspond to the reduction profile up to 400 °C carried out at a rate of heating of 11 °C/min and kept at isothermal condition for 30 min at 400 °C. The sample after TPR-I is cooled to room temperature (without exposing to air) and then a second TPR profile from room temperature to 700 °C (and isothermal

for 30 min) at the same rate of heating as in TPR-I is obtained and this profile is termed as TPR-II. The conductivity profiles of the KOH solution are recorded during the TPR run. The FID patterns of the effluents of the TPR runs are also recorded.

Activity experiments are performed in an on-line microreactor interfaced with a FID/TCD GC (Sigma Instruments, India). About 1 g of the catalyst is placed in the microreactor and then reduced in H<sub>2</sub> flow (40 ml/min) at a temperature of 400 °C for 4 h. The reactor is then cooled to the reaction temperature under H<sub>2</sub> flow and CFC-12 feed and hydrogen are passed on to the catalyst bed along with N<sub>2</sub> (to maintain required gas hourly space velocity (GHSV)). The product mixture before entering to the GC, is scrubbed with aqueous KOH (4%) solution to remove HCl/HF that are formed during the reaction. The product mixture is then analyzed using a GC with FID detector and Porapack-Q column (3 m length, 3 mm diameter SS) at an oven temperature of 120 °C. The identification of product mixture is done by micromass GC–MS (Varian 7070, UK) and major components of product mixture are identified by comparing the *m/e* values with standard *m/e* values of CFCs reported in the literature [23]. The major components of product mixture are HFC-32, CH<sub>4</sub> and unreacted CFC-12. Minor components are found to be HFC-41 and HCFC-22 depending upon the reaction conditions.

GHSV is varied from 2000 to 4800 h<sup>-1</sup> and ultra-pure nitrogen is used to maintain the GHSV. H<sub>2</sub>/CFC-12 ratios are varied in between 3 and 10. Gas flow rates were maintained by using calibrated flow meters.

### 3. Results and discussions

The BET surface area, CO uptake, MSA and PS of Pd/CCA catalysts with varying Pd loadings are given

in Table 1. The surface area of alumina decreased from 260 to 143 m<sup>2</sup> g<sup>-1</sup> during cyclohexene pyrolysis due to pore filling by carbon in the course of preparation of CCA indicating that there is no contribution of surface area by carbon. Considerable reduction in surface area of CCA occurred upon Pd loading. It can be also seen that there is no definite trend in the BET surface area of the catalysts. The BET surface area of PCCA1 and PCCA2 are almost constant, indicating that Pd continues to interact with the support in a similar way up to 4 wt.% Pd. At 6 wt.% Pd, relatively high decrease indicates pore filling by Pd crystallites. The surface area of PCCA3 and PCCA4 are again almost same and there is a decrease again in PCCA5. These results show that the interactive nature of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and non-interactive nature of carbon are both manifest in CCA support upon loading by Pd.

The 4 wt.% Pd/CCA has maximum CO uptake and also maximum MSA of 0.95 m<sup>2</sup> g<sup>-1</sup> cat., indicating the availability of maximum Pd active sites on this catalyst. As expected, Pd PSs calculated from CO-chemisorption are increasing with increase in Pd loading on CCA. The increase in Pd PS is somewhat less up to 4 wt.% Pd loading and thereafter the increase is substantial, indicating support saturation by Pd (though patchy) at 4 wt.%. Dispersion values indicate that Pd is poorly dispersed on CCA. Poorly dispersed Pd/CCA catalysts are prepared in this study by H<sub>2</sub> reduction of the catalyst at 400 °C. We followed this procedure earlier for the preparation of poorly dispersed Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/C catalysts [17]. Oxidation–reduction treatment [16] and microwave heating [15] have been reported to result in poorly dispersed Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

The XRD patterns of fresh, reduced and used catalysts are shown in Fig. 1. XRD patterns of fresh catalysts show the diffraction signals with *d* values: 1.4, 1.98, 2.37, which are attributed to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase

Table 1  
Characteristics of CCA supported Pd catalysts

Catalyst code	Pd (wt.%)	BET SA (m <sup>2</sup> g <sup>-1</sup> )	CO uptake ( $\mu$ mol/g)	D <sub>CO</sub> (%)	MSA (m <sup>2</sup> g <sup>-1</sup> cat.)	PS (nm)
CCA	–	143	–	–	–	–
PCCA1	2	135	13	6.9	0.62	17.1
PCCA2	4	131	20	5.3	0.95	22.2
PCCA3	6	115	14	2.5	0.66	47.6
PCCA4	8	114	11	1.6	0.52	80.8
PCCA5	10	91	10	1.0	0.47	111.0

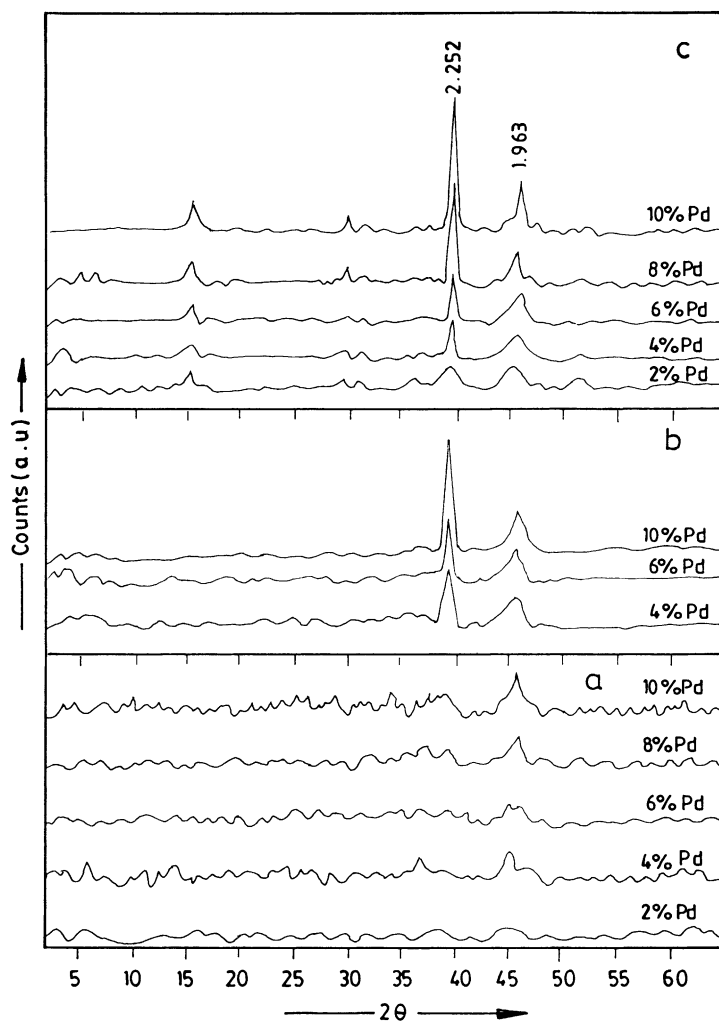


Fig. 1. XRD patterns of the Pd/CCA catalysts: (a) fresh; (b) reduced; (c) used.

and no Pd or PdCl<sub>2</sub> phases are observed in these patterns. In reduced catalysts signals due to  $\alpha$ -Pd ( $d = 1.9$  and  $2.25$ ) can clearly be seen and the intensity of this phase is found to be strongly dependent on Pd weight percent. XRD patterns of spent catalysts show that in addition to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Pd phases, a new signal (with  $d$  values of  $5.56$ ,  $1.9$  and  $1.38$ ) is observed, which corresponds to the aluminum hydroxide fluoride (Al(OH)<sub>1.96</sub>F<sub>1.04</sub>) phase and the intensity of this phase is almost constant implying that the support transformation is constant at all Pd loadings. Even though most of the alumina surface is covered by carbon during

CCA preparation by cyclohexene pyrolysis, still some of the alumina sites are available which were not accessible to aromatic/aliphatic carbon species of pyrolysis agent due to steric limitation [19]. These alumina sites uncovered by carbon reacted with small species like fluoride, generated in the course of hydrogenolysis of CCl<sub>2</sub>F<sub>2</sub> to form Al(OH)<sub>1.96</sub>F<sub>1.04</sub>.

TPR patterns of fresh CCA supported Pd catalysts are displayed in Fig. 2. A negative peak with low intensity centered at  $94^\circ\text{C}$  is observed only with PCCA1 and PCCA2. A positive peak centered at  $160$ – $210^\circ\text{C}$  can be observed in all the fresh catalysts.

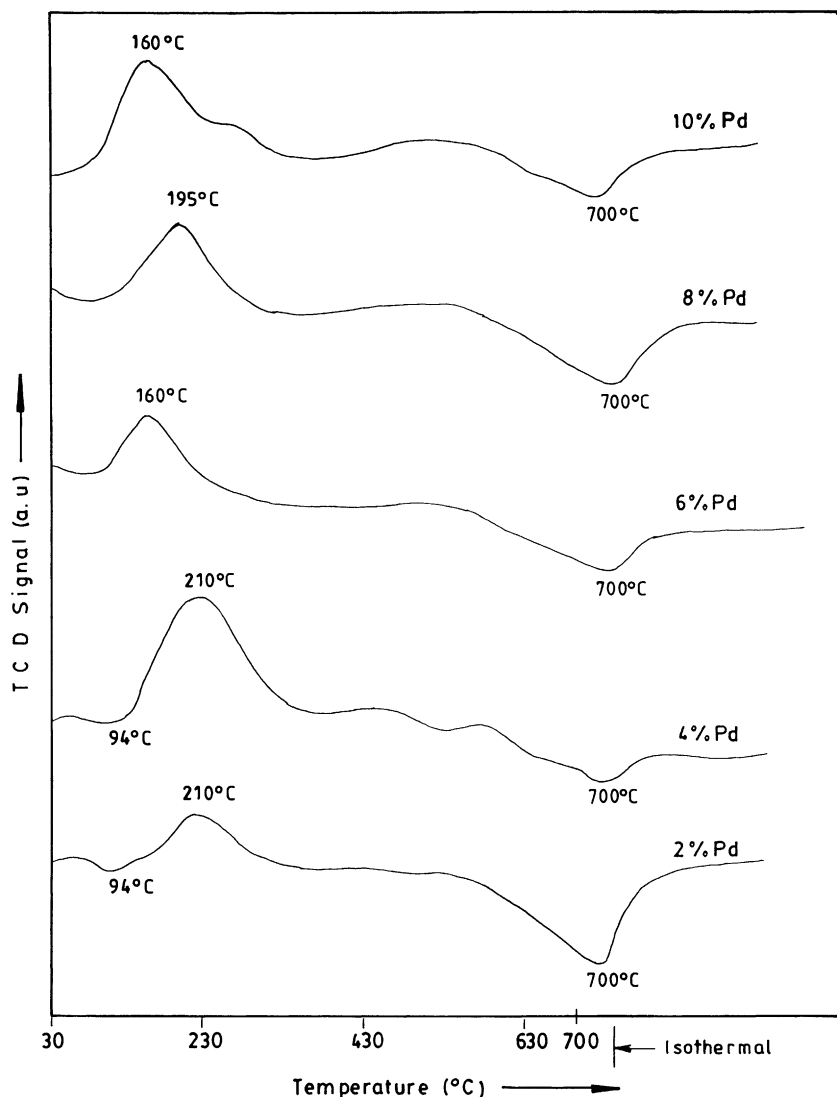


Fig. 2. TPR patterns of Pd/CCA fresh catalysts at various Pd loadings.

The  $T_{\max}$  (maximum reduction temperature) of this peak is varied in the temperature range depending upon the Pd loading in the catalyst. The intensity of this reduction peak is found to be maximum at a Pd loading of 4 wt.%. The first peak (negative) may be attributed to the decomposition of  $\beta$ -PdH<sub>x</sub>. In hydrogen atmosphere, PdCl<sub>2</sub> gets reduced easily at room temperature [11] to Pd metal (while passing reducing gas mixture prior to the start of the temperature program) and further interacts with hydrogen. This phase

is an indication of the interacting nature of the support [17,24,25]. The second peak (160–210°C) may be attributed to the consumption of hydrogen, through perhaps spill-over phenomenon, which is a feature of carbon supported catalysts [26]. This hydrogen appears to have reacted with Cl<sup>-</sup> ion which is stabilized on the catalyst surface, as carbon is known to possess a variety of functional groups like -COOH, -OH, etc. [27]. Surface oxygen functional groups, carboxylic groups and phenolic groups of the support may act

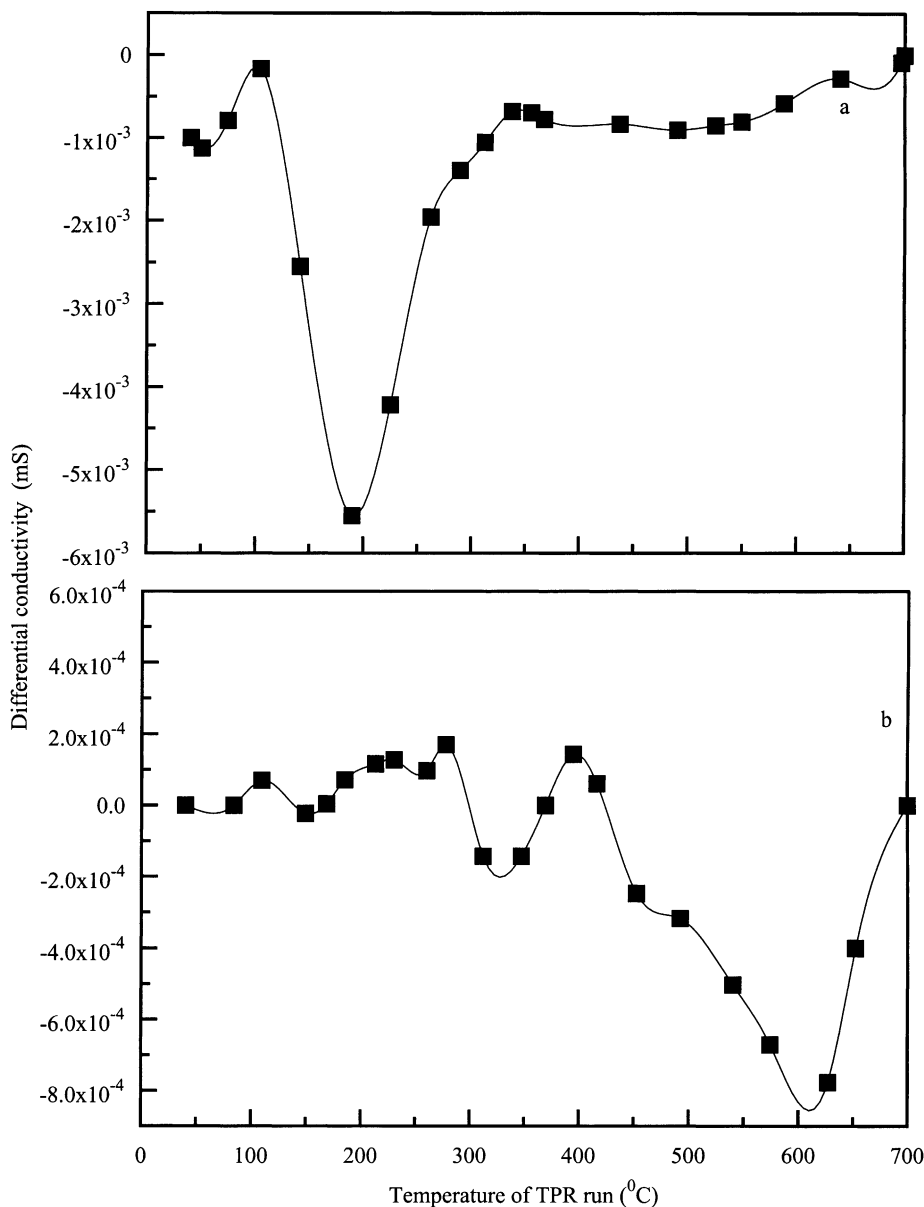


Fig. 3. Differential conductivity plots of 4 wt.% Pd/CCA catalyst obtained during the TPR experiments: (a) fresh; (b) used.

as acceptor sites for hydrogen spill-over [27]. The corresponding change in conductivity of KOH solution is also observed confirming the evolution of HCl at the peak temperature of  $\sim 190^\circ\text{C}$  (Fig. 3a). The  $\beta\text{-PdH}_x$  decomposition peak is absent in catalysts with  $>4$  wt.% Pd loading though present with a weak intensity in catalysts with  $\leq 4$  wt.% Pd. The carbon of CCA

of Pd/CCA appears to be suppressing the formation of  $\beta\text{-PdH}_x$  in fresh catalysts. Vannice and co-workers [28,29] have reported the suppression of  $\beta\text{-PdH}_x$  formation due to carbon contamination of both the bulk and surface Pd crystallites in Pd/C. Thus, the CCA supported catalyst is exhibiting both the facile reduction property of  $\text{PdCl}_2$  on alumina as well as on

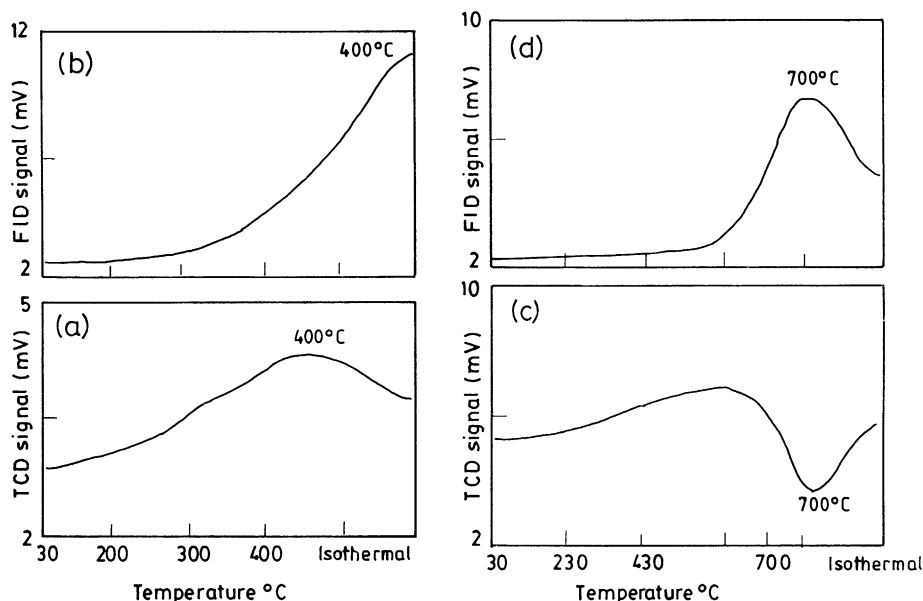


Fig. 4. TPR patterns of CCA support and corresponding FID patterns: (a) and (b) TPR-I; (c) and (d) TPR-II.

carbon supports which may influence the hydrogenolysis of CFC-12. A broad positive peak centered at  $\sim 500^\circ\text{C}$  may be attributed to gasification of carbon in CCA support. A negative peak centered at  $\sim 700^\circ\text{C}$  corresponds to the evolution of hydrocarbon which is confirmed by FID-GC analysis of the effluent of the TPR run.

To find out the nature of carbon in CCA two TPR runs (TPR-I and TPR-II) are carried out for the support. During these experiments, FID analysis of the TPR effluents have also been done along with TPR. For comparison of TPR-I and TPR-II along with FID patterns of active carbon support have also been carried out. These results are displayed in Figs. 4 and 5, respectively.

In TPR-I of the CCA support, the positive peak at about  $400^\circ\text{C}$  (Fig. 4a) may be attributed to the gasification of surface carbon of the CCA and hydrocarbon evolution can be seen from the corresponding FID pattern (Fig. 4b) of the TPR effluent. In TPR-II of the CCA support, a negative peak centered at  $\sim 700^\circ\text{C}$  (Fig. 4c) may be attributed to the desorption of heavy carbonaceous moieties ( $\text{CH}_x$ ) as is evident from the FID pattern of its effluent (Fig. 4d). The carbon species of the CCA support appear to be different from those of the active carbon support as is evident from the dif-

ferences in their TPR patterns (Figs. 4 and 5). In TPR-I and TPR-II of active carbon, positive peaks centered at  $\sim 350^\circ\text{C}$  (Fig. 5a) and at  $\sim 700^\circ\text{C}$  (Fig. 5c), respectively, can be seen. Hydrocarbon evolution at corresponding temperatures can be observed from the FID patterns of the corresponding TPR effluents (Fig. 5b and d). Both the TPR peaks may be attributed to the gasification of different carbonaceous species of active carbon.

During the preparation step of CCA support through pyrolysis of cyclohexene at  $600^\circ\text{C}$  carbon/carbon moieties ( $\text{CH}_x$ ) form on  $\text{Al}_2\text{O}_3$ , and these carbonaceous species produce hydrocarbon in the TPR experiment. The carbon present in CCA appears to be different in characteristics from the active carbon support used in preparing Pd/C catalysts [30]. Activated carbon is a high surface area material; whereas the carbon in CCA contributed to the surface area reduction of alumina, which is evident from the BET surface area of CCA and alumina (Table 1).

TPR patterns of used Pd/CCA catalysts are shown in Fig. 6. Negative peaks due to  $\beta\text{-PdH}_x$  decomposition at about  $100^\circ\text{C}$  is observed in all the catalysts. The peak intensities of  $\beta\text{-PdH}_x$  decomposition is increasing with the increase in Pd loading in Pd/CCA catalysts. It appears that Pd particles of the cata-

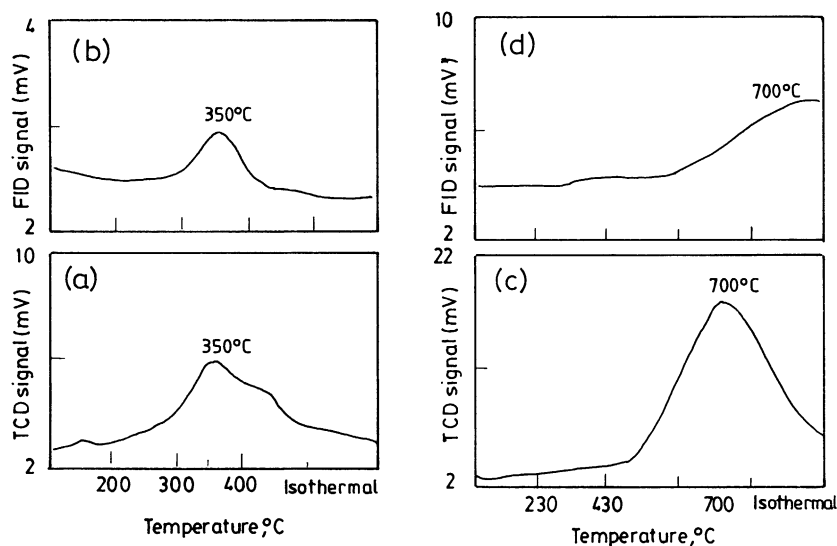


Fig. 5. TPR patterns of active carbon support and corresponding FID patterns: (a) and (b) TPR-I; (c) and (d) TPR-II.

lysts are getting reorganized through redistribution and sintering during the hydrogenolysis reaction of CFC-12 and/or in hydrogen atmosphere [31–33]. It may be mentioned here that in TPR patterns of used Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts no  $\beta$ -PdH<sub>x</sub> decomposition signal is observed at a Pd loading of 2 wt.% presumably due to partial submerging of Pd particles into the lattice of aluminum hydroxy/oxy fluoride formed during the hydrogenolysis of CFC-12 [17]. However, in used Pd/CCA catalysts signal due to the  $\beta$ -PdH<sub>x</sub> decomposition is observed even at a low Pd loading of 2 wt.% in this study. Transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in Pd/CCA to its oxy/hydroxide fluoride is also observed in the XRD patterns of used catalysts. However, it appears that carbon present in the CCA is suppressing the formation of the aluminum hydroxide fluoride with possible reduction in submerging of Pd particles into its lattice. The broad positive peak centered at around 500 °C may be attributed partly to the gasification of the carbon of the CCA support, and partly to the partial reduction of AlF<sub>x</sub> species formed during the reaction. Corresponding change in the electrical conductivity in the KOH solution can be observed in Fig. 3b (differential conductivity pattern of 4 wt.% Pd/CCA used catalyst). The partial reduction of AlF<sub>x</sub> species may be taking place at a temperature higher than that for carbon gasification with consequent ap-

pearance of differential conductivity peak at a TPR temperature of  $\sim$ 610 °C. Coq et al. [6] opined that HF was released during the final step of reduction, while preparing Pd/AlF<sub>3</sub> catalysts. The negative peak centered at  $\sim$ 700 °C in the TPR patterns of used catalysts can be attributed to the desorption of carbonaceous moiety (CH<sub>x</sub> species).

The hydrogenolysis activity of CCl<sub>2</sub>F<sub>2</sub> over 4 wt.% Pd/CCA with different space velocities is studied by keeping feed composition constant at H<sub>2</sub>/CFC-12 = 3 at a temperature of 250 °C. Fig. 7 shows the conversion of CFC-12 and selectivity to HFC-32 and CH<sub>4</sub> as a function of GHSV. At space velocities of 2400–3600 h<sup>-1</sup> the conversion is 31–38%, but selectivity towards HFC-32 is  $\sim$ 60% and that of CH<sub>4</sub> is  $\sim$ 30%. With increase in space velocity the conversion is drastically decreased to about 8% at a GHSV of 4800 h<sup>-1</sup> but selectivity towards HFC-32 is increased to about 72% and that of CH<sub>4</sub> decreased to about 25%. The selectivity to other products (CHClF<sub>2</sub> and CHF<sub>3</sub>) varied between 3 and 10% depending upon the space velocity. It is interesting to observe that there is only relatively small change in CH<sub>4</sub> selectivity with increase in GHSV emphasizing that the formation of methane is not due to the participation of HFC-32 in secondary reactions, but through an independent route [4].



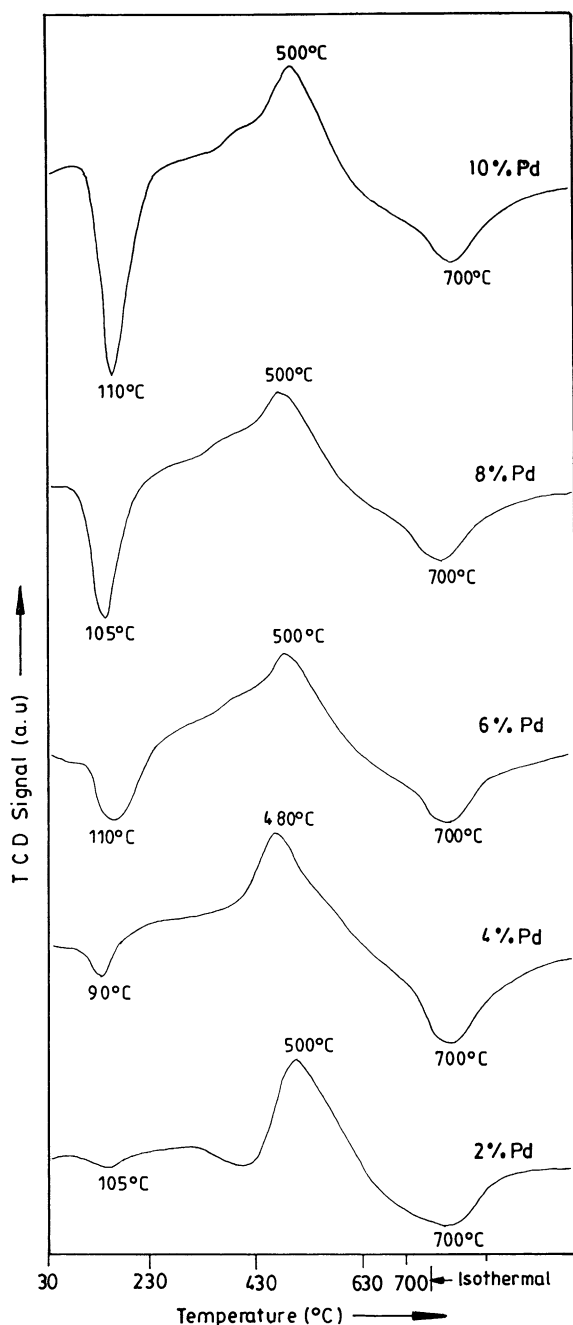


Fig. 6. TPR patterns of Pd/CCA used catalysts at various Pd loadings.

In order to find out the effect of hydrogen partial pressure on hydrogenolysis activity of CFC-12 and selectivity to HFC-32, a set of experimental runs are made by keeping GHSV constant at  $4800 \text{ h}^{-1}$  varying the reaction temperatures between 200 and  $320^\circ\text{C}$  and the  $\text{H}_2/\text{CFC-12}$  between 3 and 10. A GHSV of  $4800 \text{ h}^{-1}$  is selected because at this space velocity, the selectivity towards HFC-32 is high ( $>70\%$ ). The effect of  $\text{H}_2/\text{CFC-12}$  ratio on the activity and selectivity of 4 wt.% Pd/CCA at different reaction temperatures is depicted in Fig. 8. It can be observed from this figure that with the increase in  $\text{H}_2/\text{CFC-12}$  ratio, conversion increases up to a ratio of 8 and then decreased at all the reaction temperatures studied. The differences in conversion at different  $\text{H}_2/\text{CFC-12}$  ratios may arise out of a competitive adsorption between hydrogen and CFC molecules at different partial pressures of  $\text{H}_2$  and CFC-12 [5]. The selectivity to  $\text{CH}_2\text{F}_2$  and  $\text{CH}_4$  are strongly dependent on both  $\text{H}_2/\text{CFC-12}$  ratio and reaction temperature. At a reaction temperature of  $200^\circ\text{C}$  and a  $\text{H}_2/\text{CFC-12}$  ratio of 10, the selectivity to  $\text{CH}_2\text{F}_2$  is close to 100%, but the conversion is only about 5%. As the reaction temperature is increasing the selectivity to  $\text{CH}_2\text{F}_2$  is decreasing and that of  $\text{CH}_4$  is increasing at all  $\text{H}_2/\text{CFC-12}$  ratios. Makkee et al. [31] have reported that on Pd/C catalyst the activity and selectivity to  $\text{CH}_2\text{F}_2$  is a strong function of hydrogen to CFC-12 ratio. On palladium black, the conversion of  $\text{CCl}_2\text{F}_2$  is reported [11] to increase strongly with increase of temperature, while the selectivity to  $\text{CH}_2\text{F}_2$  is decreasing that of  $\text{CH}_4$  is increasing. It is reported that [34] Pd/C catalyst exhibited high selectivity towards  $\text{C}_2\text{--C}_3$  hydrocarbons at  $\text{CF}_2\text{Cl}_2/\text{H}_2 = 1$  and at a reaction temperature of  $250^\circ\text{C}$ . Thus, it appears that higher  $\text{H}_2/\text{CFC-12}$  ratios are preferable in improving the selectivity of desired product (HFC-32). In this study, we observed that at low  $\text{H}_2/\text{CFC}$  ratios, the adsorbed surface chloride containing radical might not be getting removed through hydrodechlorination due to insufficient surface hydrogen. Formation of  $\text{CHClF}_2$  observed in product mixture may be explained as due to associative desorption of  $^*\text{CF}_2\text{Cl}$  species with adsorbed-H species [9]. The HFC-32 selectivity increased with increase in  $\text{H}_2/\text{CFC-12}$  ratio indicating that high ratios are preferable in maximizing the HFC-32 yields and in present study, a ratio of 8 is found to produce higher yields of desired product (HFC-32).

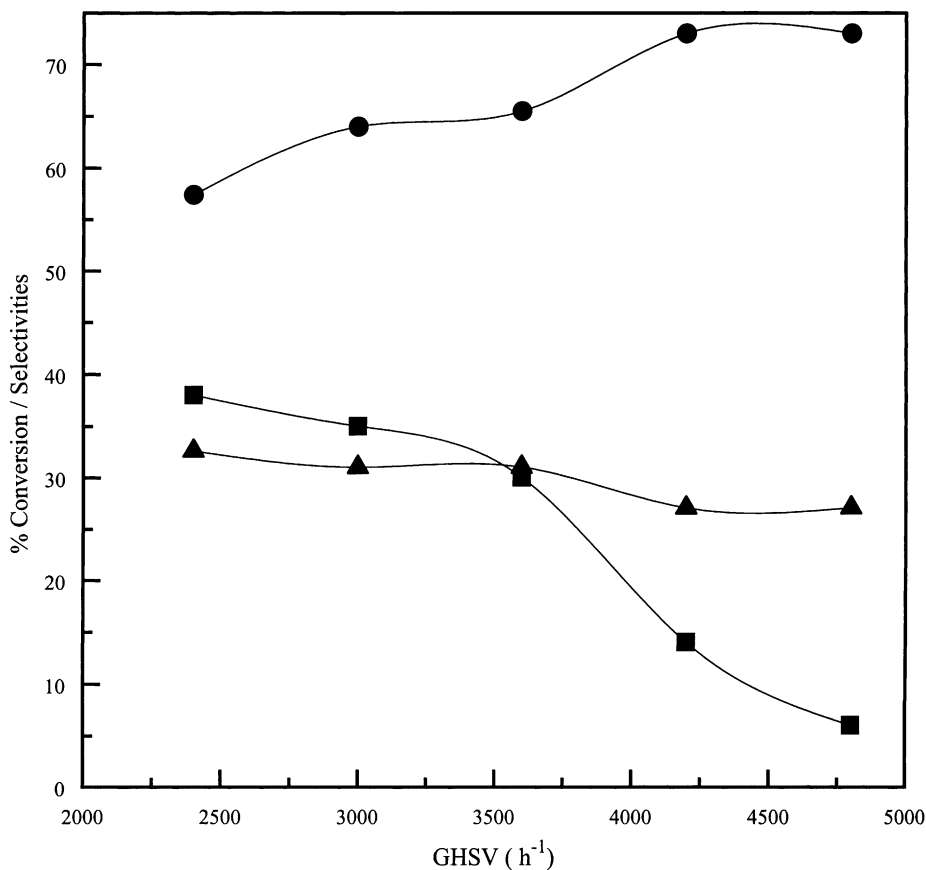


Fig. 7. Effect of GHSV on the CFC-12 hydrogenolysis activity of 4 wt.% Pd/CCA at a reaction temperature of 250 °C; H<sub>2</sub>/CFC-12 = 3: (■) conversion of CFC-12; (●) selectivity to HFC-32; (▲) selectivity to CH<sub>4</sub>.

Fig. 9 displays the CFC-12 hydrogenolysis activity at a reaction temperature of 200 °C and a H<sub>2</sub>/CFC-12 ratio of 8 during the first 160 min of reaction. The data shows that the loss of activity is negligible during the first 100 min of reaction (<5%), even though the hydrogenolysis reaction conditions are corrosive due to production of HF/HCl. In such conditions, the surface reconstruction will take place [5,6,12] and the Pd/CCA catalyst surface reconstruction in reaction medium during this period is found to be less compared to that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and active carbon supported catalysts [17]. Moreover, the selectivity towards HFC-32 is found to be maximum (100%) throughout at this reaction temperature (200 °C).

Steady state conversion and selectivity to CH<sub>2</sub>F<sub>2</sub> and CH<sub>4</sub> on Pd/CCA catalysts in hydrogenolysis re-

action of CCl<sub>2</sub>F<sub>2</sub> at different reaction temperatures are shown in Fig. 10 as a function Pd loading. The H<sub>2</sub>/CFC-12 ratio is kept constant at 8 as also the GHSV at 4800 h<sup>-1</sup>. The maximum CCl<sub>2</sub>F<sub>2</sub> conversion is observed at 4 wt.% Pd loading at all reaction temperatures. The selectivity to CH<sub>2</sub>F<sub>2</sub> is found to be close to 100% at a reaction temperature of 200 °C at all Pd loadings. However, a maximum conversion of about 25% is obtained at 4 wt.% Pd loading at this reaction temperature. At a reaction temperature of 220 °C on 4 wt.% Pd/CCA, the CCl<sub>2</sub>F<sub>2</sub> conversion is about 50%, while CH<sub>2</sub>F<sub>2</sub> selectivity is ~95% and the CH<sub>4</sub> selectivity is ~5%. On 4 wt.% Pd/CCA, the conversion increased up to ~75% with increase in reaction temperature up to 240 °C and beyond that it decreased. The CH<sub>2</sub>F<sub>2</sub> selectivity is, however, decreasing with

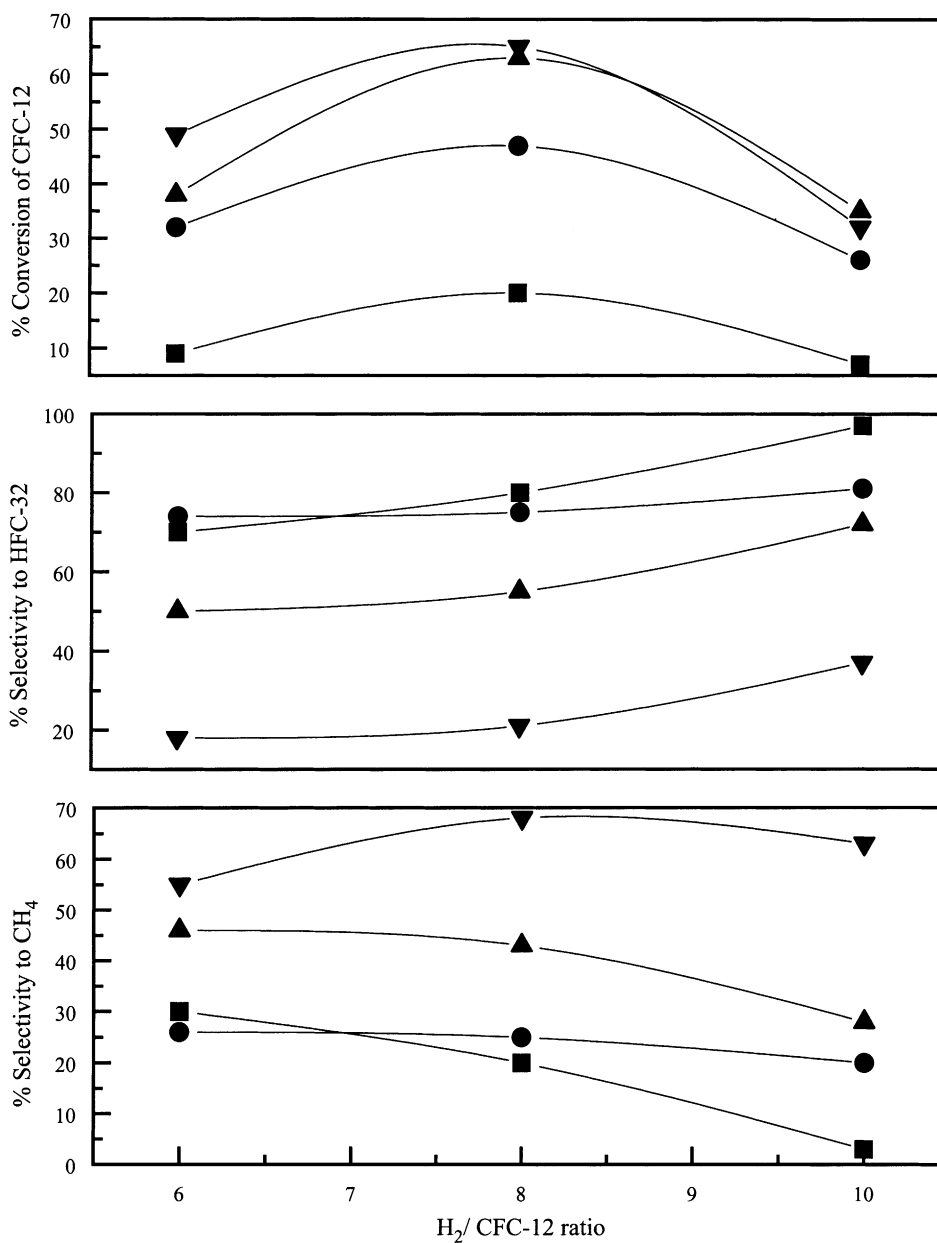


Fig. 8. Effect of H<sub>2</sub>/CFC-12 ratio on the CFC-12 hydrogenolysis activity of 4 wt.% Pd/CCA at various reaction temperatures; GHSV = 4800 h<sup>-1</sup>: (■) 200 °C; (●) 240 °C; (▲) 280 °C; (▼) 320 °C.

increase in reaction temperature and at the same time the CH<sub>4</sub> selectivity is correspondingly increasing. At 240 °C, the selectivities for CH<sub>2</sub>F<sub>2</sub> and CH<sub>4</sub> are ~65 and ~35%, respectively. Formation of CH<sub>4</sub> may be occurring independent of HFC-32 concentration. At

higher reaction temperatures ( $\geq 240$  °C) participation of HFC-32 to form CH<sub>4</sub> may also be taking place along with parallel reactions [6]. A 4 wt.% Pd loading on CCA support appears to be optimum. At this loading, the metal dispersion is also maximum. A reaction

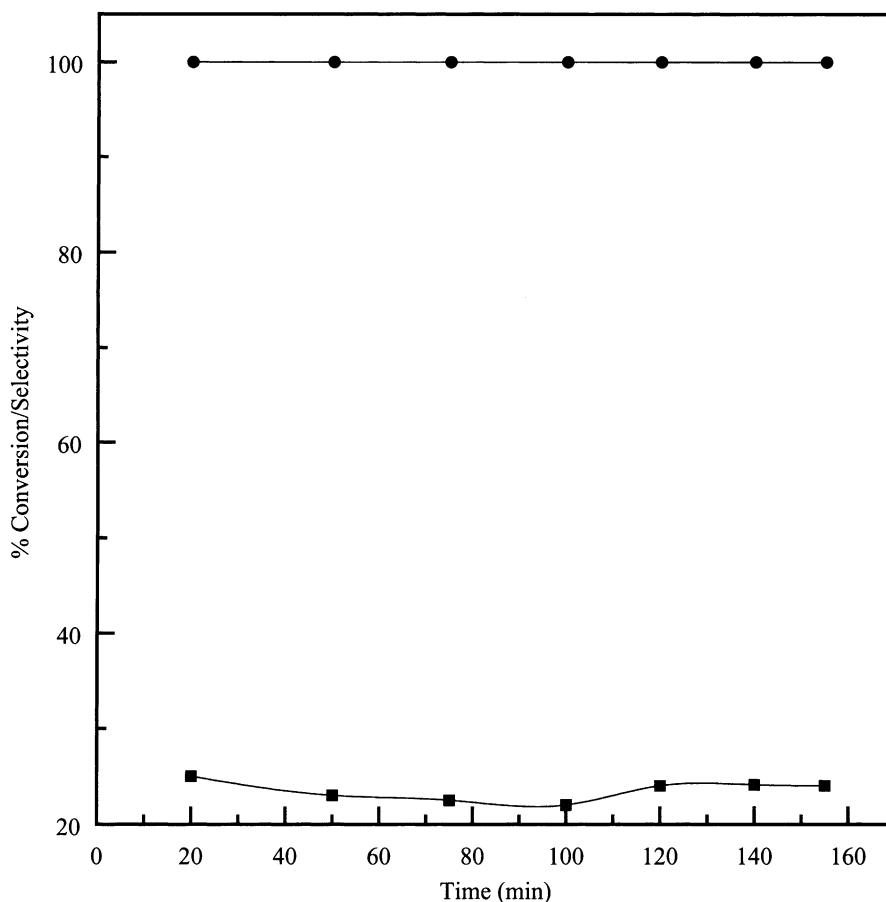


Fig. 9. Time on stream analysis of 4 wt.% Pd/CCA catalyst; reaction temperature = 200 °C;  $H_2/CFC-12 = 8$ ; GHSV = 4800 h<sup>-1</sup>: (■) conversion of CFC-12; (●) selectivity to HFC-32.

temperature of 220 °C appears to be advantageous for getting >95% selectivity for CH<sub>2</sub>F<sub>2</sub>.

At a reaction temperature of 220 °C, a GHSV of 4800 h<sup>-1</sup> and a H<sub>2</sub>/CFC-12 ratio of 8 and 4 wt.% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has shown ~50% CFC-12 conversion and 55 and 40% selectivities for CH<sub>2</sub>F<sub>2</sub> and CH<sub>4</sub>, respectively. For obtaining maximum yield of CH<sub>2</sub>F<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, 8 wt.% Pd loading is required [17]. Due to the transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into aluminum hydroxide fluoride, some of the Pd may go into lattice burial with consequent requirement of higher Pd loading for obtaining maximum activity. Similarly, under the same reaction conditions 4 wt.% Pd/C has shown a CFC-12 conversion of ~70% with a HFC-32 selectivity of ~40% and a CH<sub>4</sub> selectivity of ~55% [17].

The CCA support for Pd is thus superior to either  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or active carbon for the selective hydrogenolysis of CCl<sub>2</sub>F<sub>2</sub> to CH<sub>2</sub>F<sub>2</sub>. It appears that Pd supported on CCA is present in a more advantageous environment than that on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or activated carbon. The Pd/CCA catalyst appears to be retaining high CFC-12 conversion at lower loading of Pd associated with Pd/C and high selectivity of HFC-32 associated with Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Even so the HFC-32 selectivity is much higher on 4 wt.% Pd/CCA (~95%) than on 8 wt.% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (~75%) at a reaction temperature of 220 °C. Minimized metal-support interaction between Pd- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in CCA may be helping in preventing the Pd-lattice burial upon hydrogenolysis reaction of CFC-12 helping in getting higher HFC-32 selectivity. The electron withdrawing nature of carbon of CCA

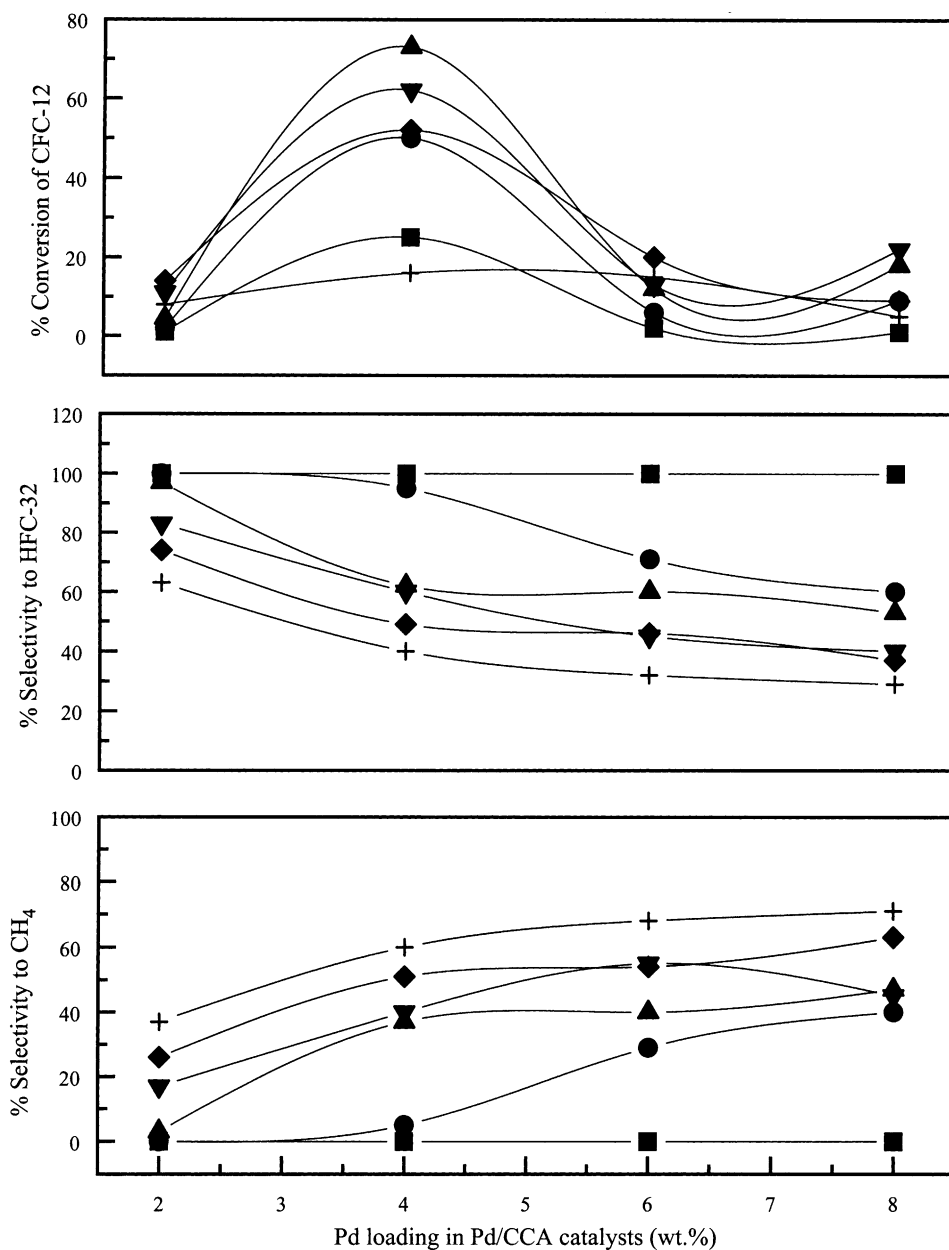


Fig. 10. Effect of Pd loading on CFC-12 hydrogenolysis activity over CCA supported catalysts at various reaction temperatures:  $H_2/CFC-12 = 8$ ;  $GHSV = 4800 h^{-1}$ : (■) 200 °C; (●) 220 °C; (▲) 240 °C; (▼) 260 °C; (◆) 280 °C; (+) 300 °C.

and low surface area associated with CCA (compared to active carbon) appear to be helpful in getting high conversion of  $CCl_2F_2$  and high selectivity for  $CH_2F_2$ .  $\gamma$ -Alumina support modification by carbon coverage is reported to improve the hydrogenation functionality

of Cu/CCA catalyst in the reaction of cyclohexanol to obtain higher selectivity towards cyclohexanone [35]. Beneficial role of carbon coverage over alumina in enhancing the aromatization selectivity of isophorone towards 3,5-xyleneol [36], in enhanced ammonia syn-

thesis activity on Ru/CCA [18,37], and improved hydrotreating process on Ni–Mo/CCA [19] are other examples.

#### 4. Conclusions

CCA prepared by pyrolysis of cyclohexene on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is used to prepare Pd/CCA catalysts. The carbon of CCA is associated with CH<sub>x</sub> moieties (as evidenced from TPR) and is somewhat different to active carbon in nature. Low dispersed Pd/CCA catalysts are obtained through hydrogen reduction at 400 °C for 4 h. The Pd/CCA catalysts have shown superior activity in the hydrogenolysis of CCl<sub>2</sub>F<sub>2</sub> and high selectivity for CH<sub>2</sub>F<sub>2</sub> compared to those on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/C catalysts. TPR of used Pd/CCA catalysts indicate the redistribution of Pd on the CCA support during the hydrogenolysis reaction. Formation of bigger crystallites of Pd during the course of reaction is further evidenced by the XRD analysis of used catalysts. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of the CCA support is also transformed during the reaction. The initial activity in the first 160 min of hydrogenolysis reaction on Pd/CCA shows that the initial loss of activity is also relatively less than that on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Pd/C. A Pd loading of 4 wt.% on CCA is found to be optimum to obtain 50% conversion of CCl<sub>2</sub>F<sub>2</sub> and a CH<sub>2</sub>F<sub>2</sub> selectivity of 95% at a reaction temperature of 220 °C, a H<sub>2</sub>/CFC-12 ratio of 8 and GHSV of 4800 h<sup>-1</sup>.

Better performance of Pd/CCA catalysts are attributed to the less interactive nature of CCA support with Pd due to the carbon coverage of alumina, there by preventing lattice burial of Pd and thus helping in maintaining high degree of selectivity towards HFC-32 at lower Pd loading compared to that on alumina and carbon. Partial hydrodehalogenation ability of this catalyst is also enhanced due to the bi-functional nature of CCA support in modifying the supported metal.

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