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Characterization and Reactivity of Pd/MgO and Pd/γ-Al_2O_3 Catalysts in the Selective Hydrogenolysis of CCl_2F_2[†]

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Al_2O_3 and MgO supported Pd catalysts with 6 wt % loading are prepared by the wet impregnation method. The catalysts are made into two parts; one of them is dried at 110 °C, and the other one is calcined at 500 °C. Conversion of CCl_2F_2 in hydrogen is carried out under identical reaction conditions on both dried and calcined catalysts after the catalysts are prereduced in H_2 at 400 °C for 3h. The fresh and the used catalysts are characterized by BET-surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption (TPD) of NH_3, and X-ray photoelectron spectroscopy (XPS). XPS data shows that surface Pd species are more in MgO supported catalyst than in Al_2O_3 supported one. In used catalysts, surface F^- concentration is more on MgO than on Al_2O_3 supported Pd catalyst. The MgO supported Pd catalyst (dried) showed higher reactivity and CH_2F_2 selectivity compared to other catalysts. MgO support is found to be superior to Al_2O_3 support for Pd for the reaction.

1. Introduction

Selective hydrogenolysis of chlorofluorocarbons (CFCs) is an important reaction, as it is one of the best routes not only for the conversion of CFCs into ozone friendly substances, but also for the synthesis of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), the elusive replacements of the ozone depleting CFCs.[1−20] Hydrodechlorination of CFCs involves the hydrogenolysis of C−Cl bond. Supported palladium catalysts are reported to be very selective and preferred catalysts for this reaction in the formation of hydrofluorocarbons, the desired products. According to Coq et al.,[10] metal fluoride supported Pd catalysts are more selective for CH_2F_2 formation in the hydrodechlorination of CCl_2F_2. Juszczyk et al.,[11] showed that the extent of hydrodechlorination of CCl_2F_2 greatly depends on Pd dispersion over Pd//γ-Al_2O_3 catalysts. Larger Pd particles are reported to be more easily transformed into Pd carbide and are more active and selective toward CH_2F_2. Makkee et al.[12,13] have studied the hydrodechlorination of CCl_2F_2 over Pd on activated carbon and Pd black catalysts and reported that PdC_x species facilitates high CH_2F_2 selectivity. Kim et al.[21] reported a long catalyst life and high selectivity to $CHCl_3$ in the hydrodechlorination of CCl_4 over Pt supported on MgO. Basicity of MgO seems to be responsible for retarding the coke formation and suppression of C_2 oligomers, which are observed to have formed in good amounts over other supported catalysts.[22] MgF_2-supported Pd is reported by Malinowski et al.,[14] to be a very stable and selective catalyst for the synthesis of CH_2F_2 (HFC-32) by the hydrodechlorination of CCl_2F_2 (CFC-12). Deshmukh and d′Itri[15] have done the transient kinetic experiments using C_2H_4 as a trapping agent for the surface carbenes and found the presence of CH_2 species in the used catalysts. Formation of propene is observed as an addition product with the addition of C_2H_4 to the surface CH_2 species.[15] The nature of the support has a great influence on the characteristics and activity of supported Pd catalysts for the hydrogenolysis of CCl_2F_2 and selectivity to CH_2F_2. The present work is aimed at the study of the conversion of CCl_2F_2 in hydrogen to selectively form CH_2F_2 over Pd supported on MgO and comparing the activity of this catalyst with that of Pd/γ-Al_2O_3 under identical reaction conditions. In this regard, Pd/MgO and Pd/γ-Al_2O_3 have been prepared and characterized both before and after the reaction by XRD, XPS, TPR, and TPD of NH_3 and BET-surface area to understand the nature and the role of the two different supports toward the selective hydrodechlorination of CCl_2F_2. The physical characteristics of the catalysts are correlated with the reactivity of the catalysts, wherever possible.

2. Experimental Section

2.1. Preparation of Catalysts. MgO and γ-Al_2O_3 supported 6 wt % Pd catalysts are prepared by the wet impregnation method using $PdCl_2$ as a precursor. Alumina, (Harshaw) with a BET- surface area of 220 m^2g^{-1} is calcined at 500 °C for 5 h in air before use. MgO is prepared by the precipitation of $Mg(OH)_2$ from aqueous $Mg(NO_3)_2$ precursor using dil. aqueous NaOH solution followed by washing with distilled water, drying overnight at 110 °C in an oven and calcination in air at 500 °C for 18 h. The BET-surface area of the MgO support thus prepared is found to be 110 m^2g^{-1}. Requisite amount of acidified (with dil. HCl) aqueous $PdCl_2$ solution is used to impregnate the support particles (18/20 BSS mesh) and the excess solution is evaporated on a water bath and then dried overnight in oven at 110 °C. The dried catalysts are made into two parts and one part of alumina supported sample is calcined at 500 °C in air for 5 h and that of MgO supported one is calcined at 500 °C in

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air for 18 h. The dried and calcined catalysts samples are reduced in hydrogen at 400 °C for 3 h before the reaction is carried out.

2.2. Characterization of Catalysts. XRD patterns are obtained on a Siemens D5000 X-ray diffractometer using Ni filtered Cu Kα radiation. Surface area measurements are made by N_2 adsorption at liquid nitrogen temperature using BET-method at 10^{-6} Torr on all-glass high vacuum system.

TPR studies are made on an on-line reactor system connected to a GC equipped with a thermal conductivity detector (TCD) and a data station for recording the TPR profiles. About 200 mg of catalyst sample is placed in the reactor and heated at a ramp of 5 °C/min from ambient temperature to 700 °C by passing the reducing gas mixture (6%H_2 in argon) over the catalyst. Prior to the start of the temperature program, the reducing gas (20 mL/min.) is passed over the catalyst for 30 min. The gas mixture from the outlet of the reactor is passed through a dilute alkali (KOH) trap to remove HCl/HF, the byproducts of the reaction, and then through a molecular sieve trap to remove the moisture. The mixture is then let into the GC column. There is a provision to analyze reduction products of the catalysts by using a flame ionization detector (FID) of the GC connected in series to TCD and for recording the profiles.

The XPS spectra are recorded on a VG Escalab 200 MK spectrometer equipped with an Al−Kα source and a hemispherical analyzer connected to a five-channel detector. During measurements the base pressure of the system is maintained around 5×10^{-10} mbar. The spectra are recorded with constant pass energy of 20 eV. Binding energies are determined by computer fitting of the measured spectra. Samples are pressed in indium foil for the study. Binding energy correction is performed by using the C 1s peak at 284.6 eV as a reference. The relative intensities of the surface composition of different elements are measured by correcting them with their corresponding atomic sensitivity factors.[23]

TPD experiments are performed using a reactor system connected to a GC equipped with a TCD, which in turn is connected to a data station. Ammonia is used as a probe molecule for evaluating the acid site distribution of the catalysts in the present study. In a typical experiment ∼250 mg of catalyst is taken in the reactor and pretreated in a flowing He at 250 °C for 2 h. After pretreatment, the temperature is brought down to 80 °C (under He flow) where the catalysts are saturated with flowing NH_3 gas for 2h. Then the catalysts are flushed with He at 100 °C for 3h in order to remove the physisorbed NH_3 on the catalyst surface. Temperature programmed desorption has been performed at a rate of heating of 5 °C/min from 100 to 500 °C. Acidity measurements are standardized by taking pulse injections of known amounts of NH_3 at the same experimental conditions.

2.3. Activity Study. Reaction of CCl_2F_2 in hydrogen over 6 wt %Pd/MgO and 6 wt %Pd/γ-Al_2O_3 (dried and calcined) catalysts is carried out in a fixed bed microreactor connected on-line to a gas chromatograph using a FID. An alkali (KOH) trap is connected to the outlet of the reactor to remove HCl and HF that form as byproducts before the product mixture is injected into the GC using a six-way sampling valve. The reactivity of the catalysts is carried out at a reaction temperature of 250 °C, a molar ratio of H_2/CFC-12 of 8, and a GHSV (gas hourly space velocity) of 4,000 h^{-1}. During a preliminary study,[24] these reaction conditions have been found to be optimum for obtaining good activity and selectivity. The products are analyzed by GC under steady-state conditions (at 4−5 h of the reaction) using a Porapak-Q (3 m long and 1/8 in. dia made of ss) column and confirmed by GC-MS analysis.

TABLE 1: BET-surface Areas and Ammonia Uptakes of the Fresh and Used Catalysts of 6 wt %Pd Supported on γ-Alumina and Magnesia

	BET-surface area (m^2g^{-1})		fresh			used		
catalyst	fresh	used	weak[a]	moderate[b]	strong[c]	weak[a]	moderate[b]	strong[c]
Pd/MgO dried	32	27	36	42	18	100	120	78
Pd/MgO calcined	41	33	42	22	16	49	65	31
Pd/Al_2O_3 dried	115	62	22	34	29	16	51	42
Pd/Al_2O_3 calcined	152	92	36	65	46	27	117	38

[a] NH_3 uptake in μmolg^{-1} in the temperature range from 200 to 300 °C. [b] NH_3 uptake in μmolg^{-1} in the temperature range from 300 to 400 °C. [c] NH_3 uptake in μmolg^{-1} in the temperature range from 400 to 500 °C.

3. Results & Discussion

3.1. BET-Surface Areas. The surface areas of the supports MgO and γ-Al_2O_3 measured by the BET-method reduced drastically after the impregnation of Pd and further the surface areas (Table 1) of the fresh catalysts are found to decrease after the reaction indicating transformation of the catalyst surface into metal fluoride or metal hydroxo fluorides that occur during the course of reaction.

3.2. XRD Results of Fresh and Used Catalysts. XRD patterns of the fresh and used Pd/Al_2O_3 and Pd/MgO catalysts are shown in Figures 1 and 2, respectively. In Al_2O_3 and MgO supported Pd catalysts in both calcined and dried forms, signals due to the support i.e., γ-Al_2O_3 ($2\theta = 66°$ with "d" value of 1.4, $2\theta = 45°$ with "d" value of 1.99 and $2\theta = 36.1°$ with "d" value of 2.46) and MgO ($2\theta = 42.3°$ with "d" value of 2.11, $2\theta = 61.5°$ with "d" value of 1.49 and $2\theta = 77.3°$ with "d" value of 1.22) & $Mg(OH)_2$ ($2\theta = 18.4°$ with "d" value of 4.77, $2\theta = 37.5°$ with "d" value of 2.37 and $2\theta = 50.4°$ with "d" value of 1.79) can be seen. No signals due to $PdCl_2$ are observed from these patterns. In used Pd/MgO and Pd/Al_2O_3 catalysts, both calcined and dried, PdC_x phases ($2\theta = 39.5°$ with "d" value of 2.303, $2\theta = 45.5°$ with "d" value of 1.991 and $2\theta = 66.5°$ with "d" value of 1.405) and α-Pd phase ($2\theta = 40°$ with "d" value of 2.25, $2\theta = 46.5°$ with "d" value of 1.95 and $2\theta = 67.9°$ with "d" value of 1.38) are observed. Juszczyk et al.[11] have reported the presence of PdC_x and AlF_x phases in used catalysts after hydrodechlorination of CCl_2F_2 over Pd/Al_2O_3. Phases due to MgO and MgF_2 are observed in Pd/MgO used catalysts. The nonstoichiometric phase due to $AlF_{1.65}(OH)_{1.35}$ xH_2O and γ-Al_2O_3 phases are found in Pd/Al_2O_3 used catalysts. Kanta Rao and co-workers[25] reported the transformation of catalyst material into metal hydroxo fluorides during the dismutation of CCl_2F_2 over alumina based catalysts and Kemnitz and co-workers[26] reported the formation of large amount of $AlF_2(OH)$ pyrochlore structure during the activation of γ-Al_2O_3 with CFC molecule in gas phase. Coq et al.[10] reported the same in the hydrogenolysis reaction of CCl_2F_2 over Pd/alumina.

3.3. TPR Analysis. *TPR of Fresh Catalysts.* Figure 3 shows the TPR patterns of fresh Pd/γ-Al_2O_3 and Pd/MgO catalysts both dried and calcined varieties. The fresh catalysts of Pd/γ-Al_2O_3 showed only a single negative peak around 90 °C, which may be attributed to the decomposition of β-PdH_x.[20,27] In hydrogen atmosphere, $PdCl_2$ or PdO gets reduced easily at ambient temperature to Pd metal[28] and further interacts with hydrogen forming β-PdH_x which appears to have occurred during the passage of reducing gas prior to the start of the

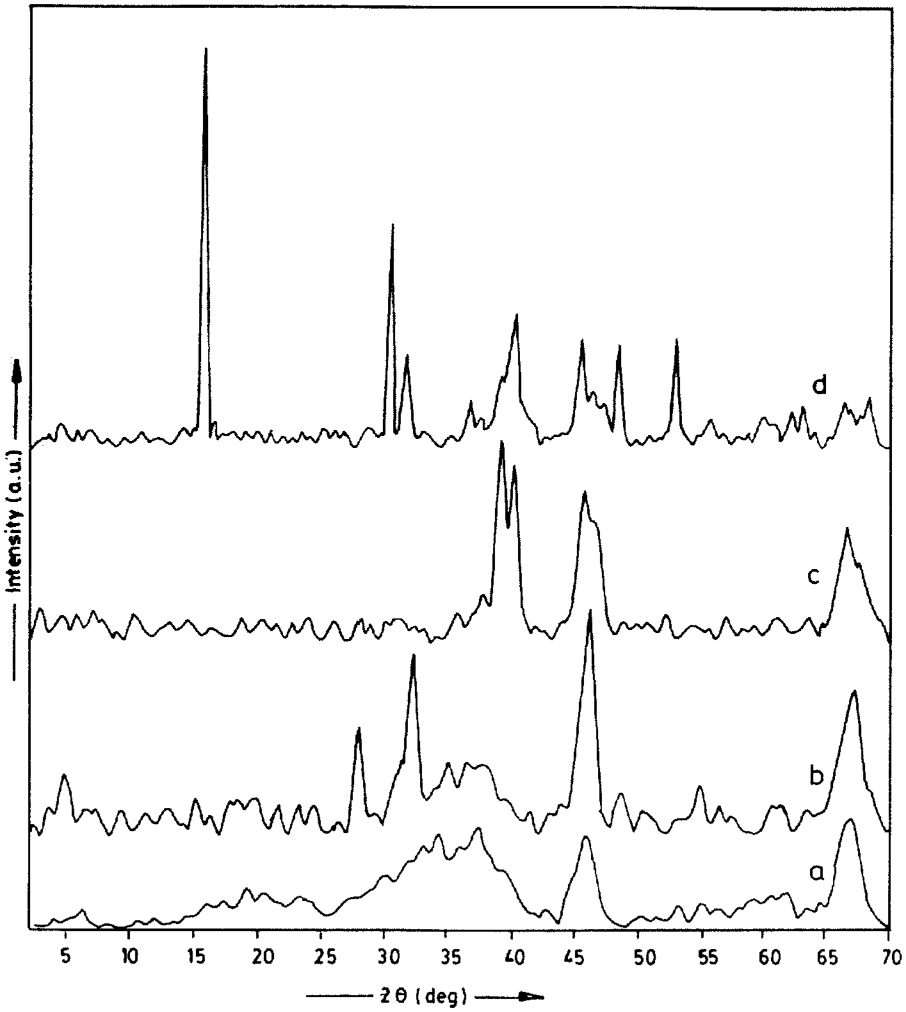

Figure 1. XRD patterns of fresh and used 6 wt %Pd/γ-Al_2O_3 catalysts (dried and calcined). (a) Pd/γ-Al_2O_3 (fresh; dried) (b) Pd/γ-Al_2O_3 (fresh; calcined) (c) Pd/γ-Al_2O_3 (used; dried) (d) Pd/γ-Al_2O_3 (used; calcined).

temperature program. The intensity of this peak is more on calcined catalyst, which may be attributed to lower Pd dispersion in this catalyst. According to Vannice et al.[29,30] in Pd supported on active carbon suppression of β-PdH_x formation is due to carbon contamination of the surface and bulk Pd (reduction of Pd particle size).

The TPR patterns of Pd/MgO fresh catalysts are found to be complex unlike the patterns of Pd/γ-Al_2O_3 fresh catalysts. No negative peak corresponding to β-PdH_x decomposition is observed over Pd/MgO fresh catalysts. One probable reason may be the high dispersion of Pd over MgO as evident from the XPS data. Increase in dispersion of Pd in Pd/SiO_2 system or decrease in Pd crystallite size is reported to result in the decrease in the intensity of β-PdH_x decomposition peak.[27]

A strong positive peak with a T_{max} at ~160 °C is observed in both dried and calcined fresh catalysts of Pd/MgO with a shoulder ~270 °C in calcined one. This peak probably corresponds to PdO reduction and/or to hydrogen consumption of metallic Pd (XPS data reveals the stabilization of some part of palladium in metallic form over MgO support) that is formed and/or hydrogen adsorption directly on MgO.[31,32] The intensity of the peak with T_{max} at ~160 °C being higher with the calcined catalyst compared to that over dried one gives credence to PdO reduction.

A negative peak centered at ~400 °C is seen in both the fresh catalysts, which may be attributed to the partial desorption of hydrogen that is chemisorbed on both palladium and magnesia. Chen et al.[33] reported to have observed two desorption peaks one at 300 °C and the other at 400 °C in the TPD of hydrogen over Pd/MgO calcined catalysts. The high-temperature positive peak above 500 °C shows further consumption of hydrogen which may be attributed to the spill over of the hydrogen activated on metallic Pd on to the MgO support.[34]

TPR of Used Catalysts. The TPR patterns of used Pd/Al_2O_3 and Pd/MgO catalysts (Figure 4) show a negative peak centered at ~100 °C both in calcined and dried forms. This peak is attributed to the decomposition of β-PdH_x.[27] Positive signals at ~425 °C in used Pd/Al_2O_3 calcined and dried catalysts can be attributed to the consumption of hydrogen by the carbonaceous species present on the catalyst surface. Evolution of CH_4 is confirmed from the FID pattern of the TPR reactor outlet stream (Figure 4c). The negative signal at ~575 °C may be attributed to the reaction of CH_x species (x $\geq$ 2) with low amount of H_2 and evolution of hydrocarbons. Negative signals centered at T_{max} ~450 °C are found in both calcined and dried used Pd/MgO catalysts. Signal centered at a T_{max} of 680 °C is present in calcined used catalyst only. These peaks may be attributed to the evolution of methane confirmed from FID pattern of the TPR reactor outlet stream and shown in Figure 4f particularly by the reduction of coke moieties (CH_x, $x \geq 2$) present on the catalyst surface. Deshmukh and d′Itri have reported the presence of surface CH_2 species in the used Pd/AlF_3 catalysts.[15]

3.4. XPS Results. Figure 5 shows the X-ray photoelectron spectra of 6 wt %Pd/γ-Al_2O_3 fresh and used catalysts in two

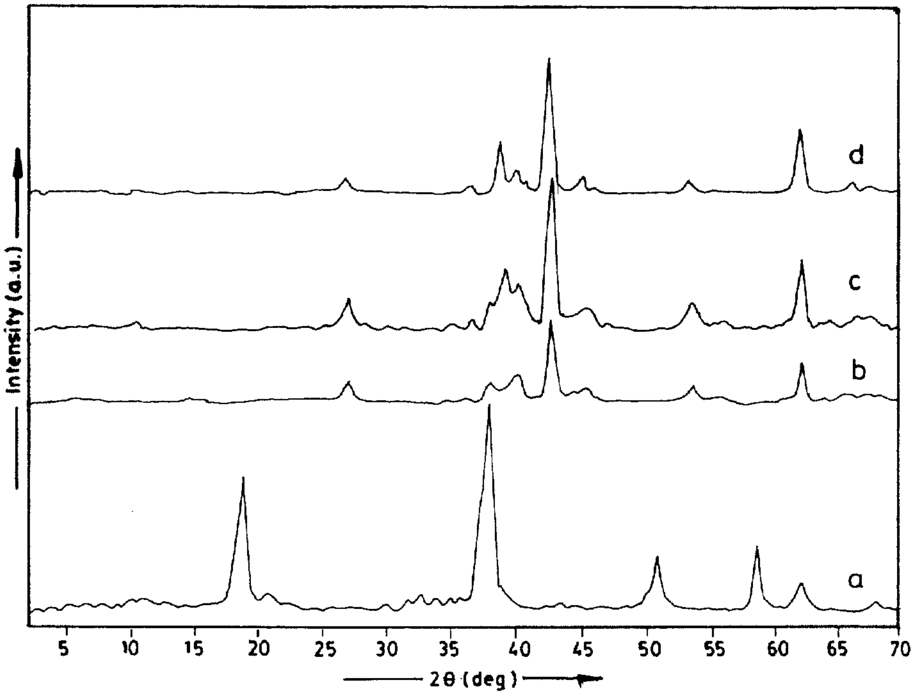

Figure 2. XRD patterns of fresh and used 6 wt %Pd/MgO catalysts (dried and calcined). (a) Pd/MgO (fresh; dried) (b) Pd/MgO (fresh; calcined) (c) Pd/MgO (used; dried) (d) Pd/MgO (used; calcined).

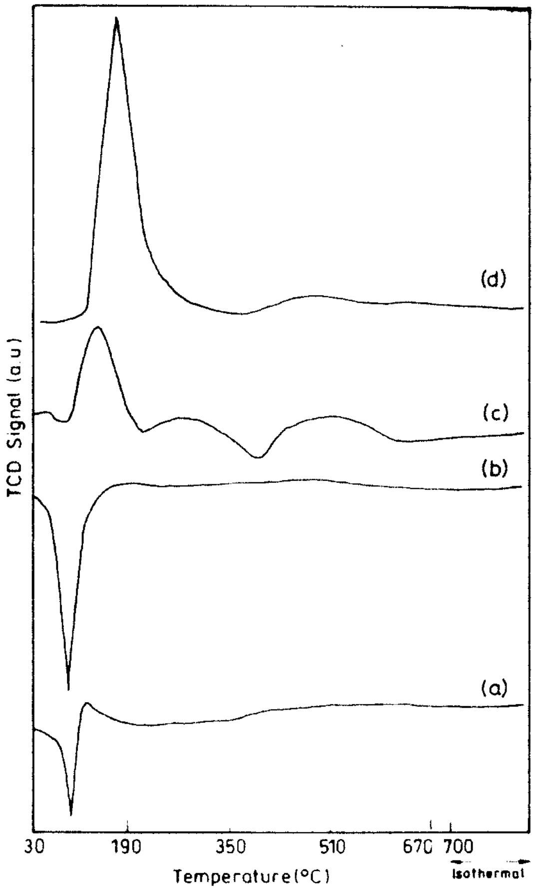

Figure 3. TPR patterns of fresh 6 wt %Pd/γ-Al_2O_3 and 6 wt %Pd/MgO catalysts. (a) Pd/γ-Al_2O_3 (fresh; dried) (b) Pd/γ-Al_2O_3 (fresh; calcined) (c) Pd/MgO (fresh; dried) (d) Pd/MgO (fresh; calcined).

different forms (dried and calcined) each. Pd/Al_2O_3 fresh catalysts (dried and calcined) showed one doublet indicating the Pd in oxide form. The Pd/Al_2O_3 dried catalyst (Figure 5a) showed a binding energy (BE) value of 337.6 eV for Pd 3d $_{5/2}$, which is close to that of $PdCl_2$ (338 eV).[35] On the other hand, the binding energy value of Pd/Al_2O_3 fresh calcined catalyst

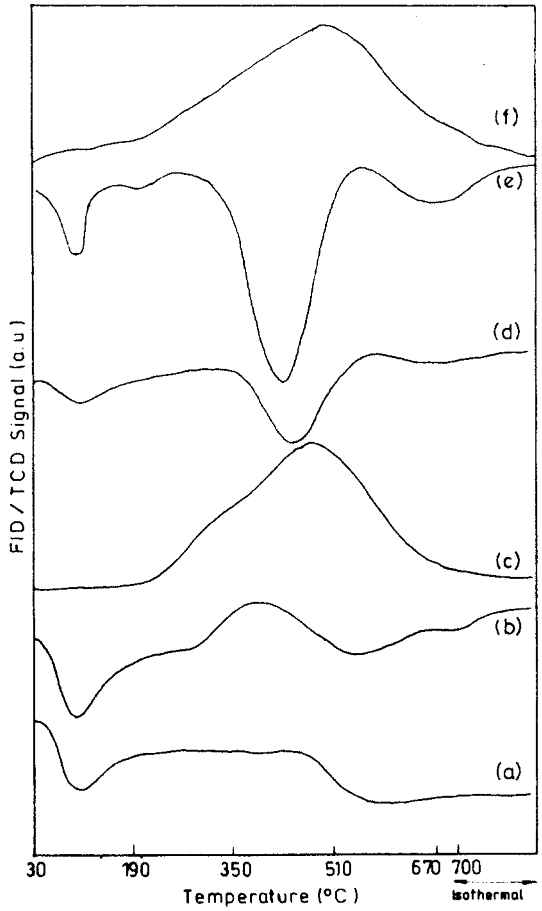

Figure 4. TPR patterns of used 6 wt % Pd/γ-Al_2O_3 and 6 wt %Pd/MgO catalysts. (a) Pd/γ-Al_2O_3 (used; dried) (b) Pd/γ-Al_2O_3 (used; calcined) (c) FID pattern of Pd/γ-Al_2O_3 (used; calcined) (d) Pd/MgO (used; dried) (e) Pd/MgO (used; calcined) (f) FID pattern of Pd/MgO (used; calcined).

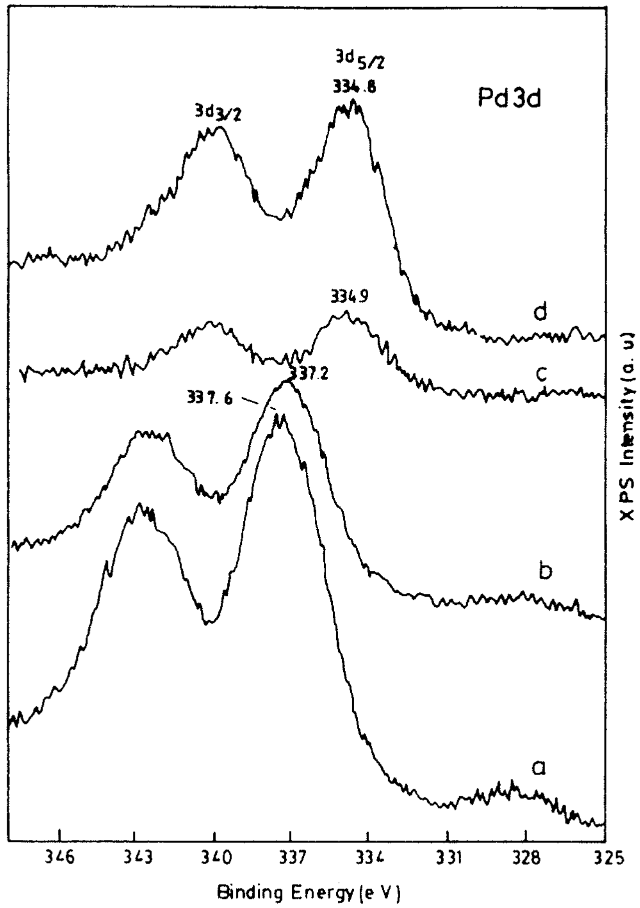

Figure 5. XPS spectra of 6 wt %Pd/ γ-Al_2O_3. (a) Pd/γ-Al_2O_3 (fresh; dried) (b) Pd/γ-Al_2O_3 (fresh; calcined) (c) Pd/γ-Al_2O_3 (used; dried) (d) Pd/γ-Al_2O_3 (used; calcined).

(Figure 5b) is at 337.2 eV indicating that Pd is in oxide form, which is logical for the calcined catalyst. The used catalysts-(Figure 5c and 5d, for dried and calcined respectively) showed the Pd $3d_{5/2}$ B. E. values of around 334.9 eV, which indicates that Pd is reduced to Pd metal during the hydrogenolysis reaction.

Figure 6 shows the XPS spectra of 6 wt % Pd/MgO fresh and used catalysts of dried and calcined forms. In Pd/MgO dried catalyst (Figure 6a) the B.E of Pd $3d_{5/2}$ is 336.0 eV and in calcined catalyst, this value is 336.9 eV with a shoulder at 335.6 eV (Figure 6b). Although the B.E. value of the dried catalyst indicates that Pd is present, mainly in metallic form, that of the calcined catalyst shows that it is predominantly present as PdO as well as metallic Pd. In dried catalyst, it might also contain some in the form of $Pd(H_2O)^{2+}$.[35] The B.E. values of Pd $3d_{5/2}$ in the Pd/MgO used catalysts are 334.6 and 335 eV for dried and calcined varieties, respectively. These values clearly indicate the existence of Pd in metallic form (B.E. value of Pd $3d_{5/2}$ in metallic form is 335.2 eV). The B.E. values of Pd $3d_{5/2}$ show that Pd is stabilized to some extent in the form of metal over MgO supported fresh catalysts and on the other hand as Pd^{2+} over alumina supported fresh catalysts.[36,37]

On comparison of Al 2p and Mg 2p B.E. values of fresh and used catalysts, the extent of fluorination appears to be higher over MgO than on alumina. The B.E. of Mg 2p of fresh Pd/MgO is shifted from 49.8 eV to 50.8 eV[23] in used catalysts (not shown in figure) indicating that MgO is transformed partially to MgF_2. Similarly, the B.E. values of Al 2p in fresh Pd/alumina catalysts (74.4 eV) are changed to 74.8−75.2 eV in used catalysts (not shown in figure), which are intermediate between the B.E. values of Al 2p in oxides (74.2−74.6 eV) and AlF_3 (76.1−77.0 eV),[23] indicating the transformation of alumina to perhaps aluminum hydroxo fluoride.

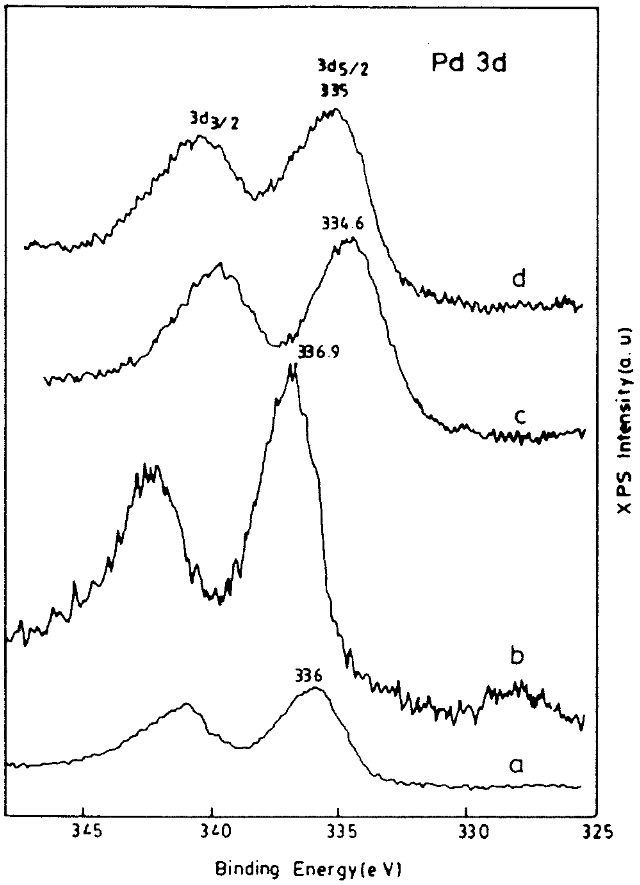

Figure 6. XPS spectra of 6 wt %Pd/MgO. (a) Pd/MgO (fresh; dried) (b) Pd/MgO (fresh; calcined) (c) Pd/MgO (used; dried) (d) Pd/MgO (used; calcined).

The F 1s B.E. values have been reported by Kemnitz et al.[38] to be in the range of 687.0 to 687.8 eV for $AlF_{2.3}(OH)_{0.7}\cdot H_2O$ and β-AlF_3 catalysts from the XPS analysis of these samples. The F 1s B.E values over Pd/Al_2O_3 used catalysts are found to be 686.4 eV and 685.5 eV (not shown in the figure) in the dried and calcined ones, respectively. These values also suggest the possible formation of aluminum hydroxo fluoride from alumina during the course of the reaction (with the release of HF). The F 1s spectra of Pd/MgO used catalysts (not shown in the figure) showed the photo peaks at B.E values of 685.5 and 685.4 eV for dried and calcined catalysts, respectively. These values confirm the transformation of MgO to MgF_2.

The surface compositions of Pd/Al, Pd/Mg, F/Mg, F/Al, and Pd/C ratios are presented in Table 2. The ratios have been calculated from the relative intensities obtained from corrected XPS of Pd 3d, F 1s, Mg 2s, Al 2p, and C 1s (by their corresponding atomic sensitivity factors as cited in the literature).[23] Even though Pd loading of 6 wt % is maintained in all the catalysts, it is evident from Table 2 that Pd is in more dispersed state on MgO surface than on alumina in both fresh and used catalysts. The F/Al ratio (F/Al < 3) indicates a partial transformation of alumina to hydroxo fluorides. On the other-hand, the F/Mg ratio, which is found to be >2, suggests high enrichment of fluoride on Pd/MgO catalyst surface during the course of hydrogenolysis reaction. The apparent surface enrichment of fluoride in used Pd/MgO catalysts beyond a F/Mg ratio of 2 may be attributed to the deposition of heavy halogenated hydrocarbons on the surface of the catalyst during the hydro-

TABLE 2: Surface Compositions of the Pd, Al, Mg, C, and F Calculated from the XPS Analysis of the Fresh and Used Al_2O_3 and MgO Supported 6 wt %Pd Catalysts

catalyst	Pd:Al	Pd:Mg	F:Al	F:Mg	Pd:C
Pd/Al_2O_3 dried; fresh	0.0308				
Pd/Al_2O_3 calcined; fresh	0.0157				
Pd/Al_2O_3 dried; used	0.0050	-	1.1016	-	0.0461
Pd/Al_2O_3 calcined; used	0.0139	-	1.1671	-	0.0905
Pd/MgO dried; fresh		0.0438			
Pd/MgO calcined; fresh		0.0459			
Pd/MgO dried; used		0.0246		3.6510	0.1121
Pd/MgO calcined; used		0.0243		3.5740	0.1326

genolysis of CCl_2F_2. Wiersma et al.[13] reported the presence of heavy halogenated hydrocarbons in used Pd/C catalyst after the hydrodechlorination of CCl_2F_2. It appears that the extent of heavy halogenated hydrocarbons present in used Pd/MgO is higher than that present in used Pd/Al_2O_3.

3.5. Acidity Results. During the hydrogenolysis of CCl_2F_2 on supported Pd catalysts, change is expected not only in the structure of Pd (due to the formation of PdC_x species), but also in the support structure (due to the transformation of oxide supports to halides or oxyhalides by the release of HF/HCl during the reaction). Thus, there is every possibility of change in the acid site distribution of the catalyst after the reaction. This may affect the product distribution during time on stream analysis of the reaction until the catalyst is fully stabilized in the corrosive atmosphere of hydrogen halides. Knowledge of the variation in the acid site population of catalysts before and after reaction may throw some light in assessing the product composition at steady-state conditions as well as at the start of the reaction. Temperature programmed desorption (TPD) of NH_3 is a well-known technique in finding out the acid site population present in the catalyst.[39] The acid site population of fresh and used alumina and magnesia supported Pd catalysts are shown in Table 1. All the catalysts show an increase in the number of acid sites of all the strengths when hydrogenolysis reaction of CCl_2F_2 is carried over them.

The extent of increase in the number of acid sites is more in used Pd/MgO (dried) catalyst than in calcined one unlike in used Pd/Al_2O_3 catalysts, where there is only a marginal increase after the reaction. In Pd/MgO, the support is perhaps more fluorinated compared to that of Pd/Al_2O_3, which might have been partially fluorinated. This fact is further confirmed from XRD and XPS results of the fresh and used catalysts. In dried catalyst, the easier exchange of hydroxyl groups on magnesia by F^- is expected as magnesia gets transformed to brucite in aqueous medium during the preparation step. Transformation of periclase to brucite in aqueous medium is easy[40] and also the exchange of O^{2-} and OH^- on magnesia by Cl^- is documented.[41] Thus, easier transformation of $Mg(OH)_2$ to MgF_2 in the presence of HF can be expected over Pd/MgO dried catalysts getting highly fluorinated. The fluoride ligands surrounding the metal cations are known to exhibit higher Lewis acidity than oxides or hydroxides,[42,43] thus hydroxo fluorides can be expected to show lower Lewis strength than fluorides. It is worth noting that strong acid sites on Pd/alumina fresh and used are more than in the fresh and used Pd/MgO catalysts, with the exception of Pd/MgO used dried catalyst. The lower acidity in Pd/Al_2O_3 used catalysts compared to that in Pd/MgO used catalysts may be due to the carbonaceous deposits on the former in more quantities than on the later. It is reported that carbon coverage occurred during the aromatization reaction on alumina drastically reduces its acidity.[44]

TABLE 3: Hydrodechlorination of CCl_2F_2 over 6 wt % Pd Supported on MgO and γ-Al_2O_3, Calcined and Dried Catalysts at a Reaction Temperature of 250 ×bcC, GHSV of 4,000h^{-1} and H_2/CCl_2F_2 of 8

catalyst	% conversion of CCl_2F_2	% selectivities				
		CH_2F_2	CH_4	CH_3F	$CHClF_2$	others
Pd/MgO dried	70	64.3	32.6	-	-	3.1
Pd/MgO calcined	58	63.6	29.2	3.1	-	4.1
Pd/Al_2O_3 dried	27	45.6	49	-	1.8	3.6
Pd/Al_2O_3 calcined	50	52.4	37	3.0	5.0	2.6

Kemnitz et al.[26] reported MgF_2 to have shown lower amounts of NH_3 desorption as compared to AlF_3 and other Mg doped AlF_3 compounds. They have also shown MgF_2 to possess a sufficient amount of Lewis acid sites, which are different in strength from the sites observed over AlF_3. Differences in the acidity of Pd/alumina and Pd/magnesia used catalysts observed in this study vis-à-vis to that reported by Kemnitz et al. may arise out of the differences in the nature of catalyst, nature of reaction conditions as well as reaction duration.

3.6. Activity Results. The product distributions on different catalysts recorded at steady-state conditions are presented in Table 3. The initial activity measurements are also discussed in order to explain the formation of various other products during the course of the reaction. The time on stream analysis of the products is given in Figure 7. The steady-state is attained at 4−5 h of the reaction in the hydrogenolysis of CCl_2F_2 over all the catalysts studied. From Figure 7, it can be observed that the selectivity to CH_4 decreased from ∼45% to ∼30% with time over Pd/MgO catalysts. However, on Pd/Al_2O_3 catalysts, there is an initial decrease in the first hours of reaction, and thereafter, the selectivity to CH_4 is stabilized at ∼40−50%. Formation of CH_4 occurs through defluorination of CCl_2F_2 to CCl_2F (intermediate species) and subsequently by dechlorination to yield CH_4. Although the selectivity to CH_2F_2 is about the same (∼64%) on both dried and calcined Pd/MgO catalysts, the conversion of CCl_2F_2 is higher (70%) in dried catalyst than that (58%) on calcined one. However, it is different on γ-Al_2O_3 supported Pd catalysts. Although the conversion is higher on calcined catalyst, it is much lower than those on MgO supported Pd catalysts. The selectivity to CH_2F_2 is also lower (45−53%) on alumina supported catalysts. Under the corrosive reaction conditions where HF/HCl are formed during the course of reaction, support transformation into respective metal oxy/hydroxo fluorides or fluorides would be expected. Formation of the main desired product CH_2F_2 is dependent on the desorption rates of intermediate species $:CF_2$ from catalyst surface. It is also reported that support surfaces with Lewis acid sites induce electron deficient/vacant sites on Pd surface.[10] The formation of byproduct $CHClF_2$ (R-22) is observed only on Al_2O_3 supported catalysts. CH_3F (R-41) is formed over both Pd/MgO and Pd/Al_2O_3 calcined catalysts. Although $CHClF_2$ forms via the adsorbed $[CClF_2]^*$ intermediate species, formation of CH_3F may occur via hydrodefluorination of $[:CF_2]^*$ intermediate to adsorbed $[:CHF]^*$ species and subsequent hydrogenation to yield CH_3F.[10] No halogen exchange products namely $CClF_3$ and CCl_3F are observed in this study.

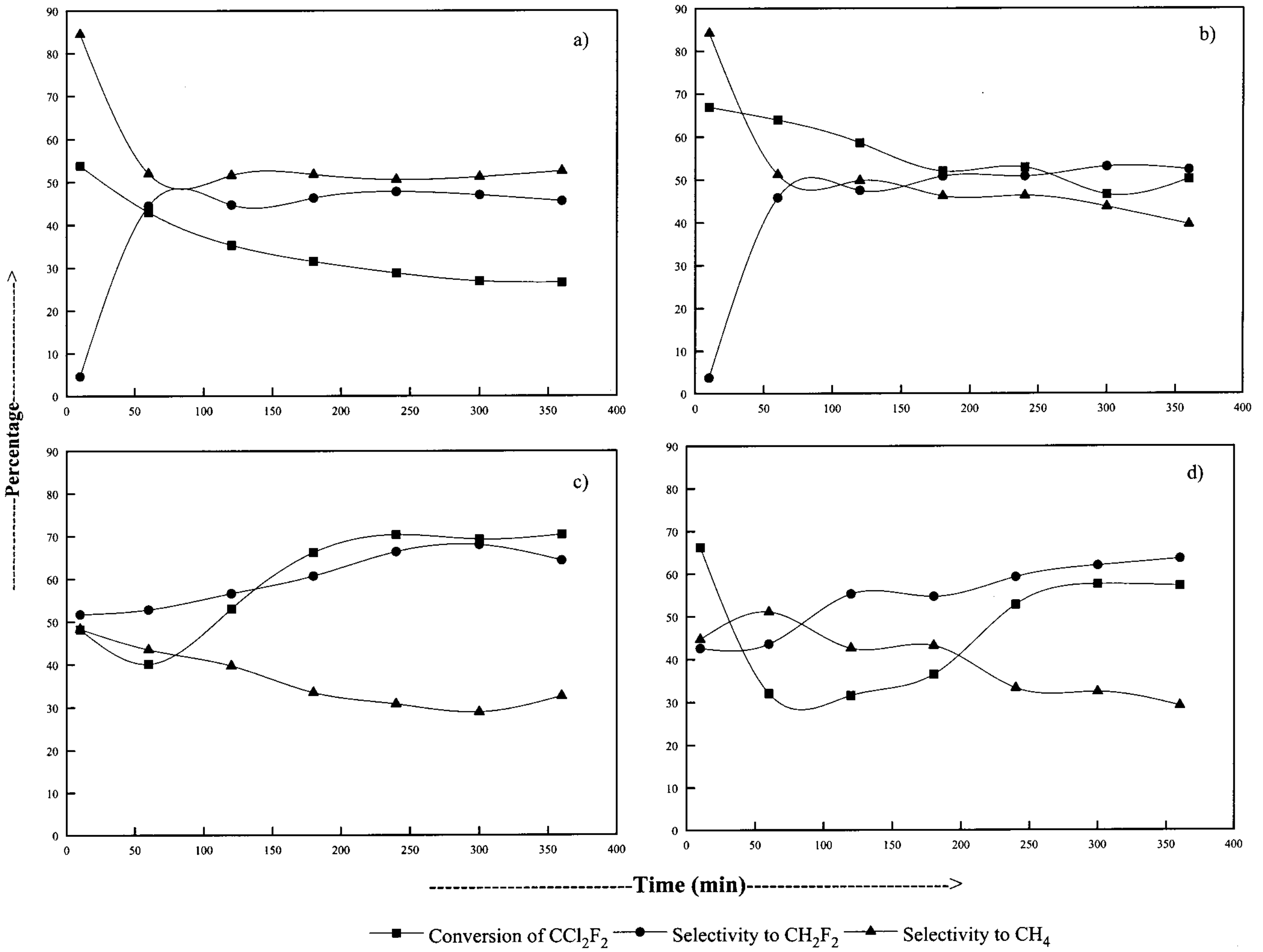

Figure 7. Time-on-stream activity of CCl_2F_2 conversion in hydrogen over dried and calcined 6 wt %Pd/MgO and 6 wt %Pd/γ-Al_2O_3 catalysts. (a) Pd/γ-Al_2O_3 (dried) (b) Pd/γ-Al_2O_3 (calcined) (c) Pd/MgO (dried) (d) Pd/MgO (calcined).

The surface compositions of the catalysts with respect to Pd/Al and Pd/Mg ratios (Table 2) are obtained from the XPS analysis of the fresh and used catalysts. It can be seen that Pd/Mg ratios are more or less same in calcined and dried catalysts. However, in Pd/Al_2O_3 catalysts the Pd/Al ratio is 3 times more in the calcined catalyst than that in dried catalyst. The transformation of catalyst surface occurs during the initial activity through reaction of the catalysts with by-products of reaction, HCl and HF. The XPS data of the used Pd/MgO dried catalyst show that F/Mg ratio is >3, which is nearly three times higher than that on Pd/Al_2O_3 used catalyst (F/Al ~ 1.1). TPR analysis of the used catalysts revealed that the amount of coke deposition is more over Pd/MgO calcined than that on the dried used catalyst. Pd/MgO dried catalyst which shows highest increase in acidity upon reaction, has also exhibited highest activity and good CH_2F_2 selectivity among the catalysts studied probably on account of more electron deficient character of Pd in this catalyst.

4. Conclusions

MgO supported Pd catalysts have shown higher hydrogenolysis activity for CCl_2F_2 and selectivity to CH_2F_2 (R-32) compared to those on Al_2O_3 supported Pd catalysts. This behavior can be attributed to higher dispersion of Pd on MgO surface than on Al_2O_3 surface and also to the presence of higher amounts of F^- in MgO supported Pd catalysts (occurred during the hydrogenolysis reaction) compared to that on Al_2O_3 supported Pd catalysts. The nature of carbonaceous deposits occurred during the reaction appears to be dissimilar on both the supported catalysts. XRD analysis of the used catalysts indicated the presence of $AlF_{1.65}(OH)_{1.35}\ xH_2O$ phase over Pd/γ-Al_2O_3 used catalysts and MgF_2 phase on Pd/MgO used catalysts due to surface transformation during the course of reaction. XPS data shows that Pd is present in different environments on Al_2O_3 and MgO supports, respectively. Surface Pd concentration is more on MgO than on Al_2O_3. During the course of hydrogenolysis reaction, there is more surface enrichment of fluoride on MgO than on Al_2O_3 support. The relative enhancement in the acidity upon hydrogenolysis reaction is highest on dried Pd/MgO catalyst. Another probable reason for higher acidity on Pd/MgO used catalyst may be that the extent of coking is higher on Pd/Al_2O_3 used catalyst resulting lower acidity.

Among the catalysts studied, Pd/MgO, dried variety has shown highest hydrodechlorination activity with high CH_2F_2 selectivity. Pd//γ-Al_2O_3 catalysts, though have shown different activities, the selectivities to CH_2F_2 and CH_4 are around 40–50%.

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