

Role of hydrotalcite precursors as supports for Pd catalysts in hydrodechlorination of CCl_2F_2

A.H. Padmasri, A. Venugopal, V. Siva Kumar, V. Shashikala, B.M. Nagaraja, P. Seetharamulu, B. Sreedhar, B. David Raju, P. Kanta Rao, K.S. Rama Rao*

Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, Andhra Pradesh, India

Received 10 February 2003; received in revised form 1 September 2003; accepted 12 September 2003

Available online 15 September 2004

Abstract

The selective synthesis of CH_2F_2 by the hydrodechlorination of CCl_2F_2 is studied over calcined Mg–Al and Mg–Cr hydrotalcites (CMA-HT and CMC-HT) supported Pd catalysts. Their activities are compared with the corresponding oxides, viz., MgO, $\gamma\text{-Al}_2\text{O}_3$ and Cr_2O_3 supported Pd catalysts. Pd catalyst on the support from Mg–Al HT precursor is found to be superior and advantageous in terms of higher selectivity towards CH_2F_2 formation and stability of the catalyst. The catalysts followed the order: Pd/CMA-HT > Pd/MgO > Pd/ $\gamma\text{-Al}_2\text{O}_3$ > Pd/ Cr_2O_3 > Pd/CMC-HT in terms of the selectivity towards CH_2F_2 formation. Pd/CMC-HT showed deeper hydrogenation activity towards the formation of CH_4 . Pd/CMA-HT and Pd/MgO showed a higher increase in the acidity of the catalyst after the reaction, which facilitates to maintain the Pd site in electron deficient environment and thereby yielding higher selectivity towards CH_2F_2 . The lack of sufficient acidity on Pd/CMC further explains the poor selectivity to CH_2F_2 observed over this catalyst. XPS results also confirm the enrichment of surface fluoride over Pd/CMA-HT and Pd/MgO used catalysts.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrotalcite; MgO; CMA-HT; CMC-HT; Hydrodechlorination; CCl_2F_2 ; CH_2F_2

1. Introduction

Hydrotalcites (HTs) are a well-known class of compounds for their versatility in catalyzing various types of reactions. Hydrotalcites are less extensively studied as supports in catalyzing vapour phase heterogeneous reactions. Recently we found HTs [1,2] as good supports for Pd catalysts in the hydrodechlorination of CCl_2F_2 to CH_2F_2 . Coq and coworkers [3] have also shown Pd-hydrotalcite as a good catalyst for this reaction.

The ban on CFCs resulted in the need for the eradication of existing feedstocks that are still causing the destruction of ozone layer and also in synthesizing their alternatives. The development of CFC alternatives has been focused on non-chlorinated compounds with similar physical properties that

would break down in the lower atmosphere. One such class of alternatives is the hydrofluorocarbons (HFCs) and the simplest method to obtain them is by the selective hydrogenolysis of CFCs on metal surface with selective chlorine removal, which is called the hydrodechlorination.

Supported palladium catalysts are well documented in various reports in the selective synthesis of HFCs from CFCs by hydrodechlorination route [4–15]. Most commonly reported supports are $\gamma\text{-Al}_2\text{O}_3$, activated carbon, AlF_3 or fluorinated aluminas. The basic reason behind using oxides or fluorides is explained as to enhance the electron deficiency of Pd through the Lewis acidity of the supports. Coq et al. [5] explained the reason as the easier desorption of the $:\text{CF}_2$ species, which is found to be a key intermediate in governing the selectivity of desired product, CH_2F_2 in the hydrodechlorination of CFC-12 (CCl_2F_2) from the surface of more electron deficient Pd. However, higher Lewis acidity of AlF_3 or Al_2O_3 type supports can lead to fast deactivation of catalysts and supports

* Corresponding author. Fax: +91 40 27160921.

E-mail address: ksramarao@ins.iictnet.com (K.S. Rama Rao).

of carbon suffer from poor selectivity to desired product with higher dispersion of active component, Pd over it leading to the formation of deeper hydrogenation product, CH₄. Also, this support offers poor mechanical strength to the catalyst. Hence, there is a need to look for alternative supports.

Basic carriers such as MgO, calcined Mg–Al HT and calcined Mg–Cr HT are found to show stable and higher activity towards the formation of CH₂F₂ in our earlier studies [15,1,2]. The present work is aimed at the study on the comparison of the hydrodechlorination activity of CCl₂F₂ over two different Pd supported on calcined HT systems namely Mg–Al and Mg–Cr HTs with their individual oxide supports, viz., MgO, γ -Al₂O₃ and Cr₂O₃.

2. Experimental

2.1. Preparation of catalysts

A Pd loading of 6 wt.% was deposited by wet impregnation method over five different supports, γ -Al₂O₃ (commercial, Harshaw), MgO (prepared by precipitation from Mg(NO₃)₂ using aqueous NaOH solution), Cr₂O₃ (from Cr(NO₃)₃ by precipitating with liquid NH₃), mixed oxides of MgO–Al₂O₃ (CMA-HT) and MgO–Cr₂O₃ (CMC-HT) obtained from their corresponding hydrotalcite precursors. Earlier studies [2] indicated a Pd loading of 6 wt.% to be optimum for obtaining good activity and selectivity in the hydrodechlorination of CCl₂F₂ to CH₂F₂. The Mg–Al and Mg–Cr HTs were prepared by Reichle's method [16] and the details of the preparation were reported elsewhere [1,2]. These hydrotalcites were then decomposed at 450 °C for 18 h in presence of air in case of Mg–Al HT and in N₂ with Mg–Cr HT to yield CMA-HT and CMC-HT supports, respectively.

2.2. Characterization of catalysts

All the fresh and used catalysts have been characterized by BET-surface area measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR) and temperature programmed desorption (TPD) of NH₃. BET-surface areas were measured on an all glass high vacuum system by N₂ adsorption at 10⁻⁶ Torr vacuum at –196 °C. Powder X-ray diffraction patterns of the catalysts were recorded on a Siemens X-ray diffractometer using Ni-filtered Cu K α radiation. TPR profiles of the samples were generated on a home-made on-line reactor system which is connected to a gas chromatograph equipped with a thermal conductivity detector (TCD) coupled to a flame ionization detector (FID). The patterns were taken from ambient temperature to 700 °C at a heating ramp of 5 °C/min. and kept at the final temperature isothermally for about 30 min. The same system was used for the TPD experiments using ammonia as the probe molecule for evaluating the acidities of the catalysts in the temperature range of 100–500 °C at a heating rate of 5 °C/min. A data station

with standard GC software was used to record the TPR and TPD patterns. The details of the TPR and TPD experiments were discussed in our earlier report [15]. The surface analysis of the catalysts by XPS was done on a KRATOS Axis 165 Photoelectron Spectrometer equipped with an Mg K α source. The binding energy correction was performed by using the C 1s peak at 284.6 eV as a reference for all the elements recorded. The relative intensities of the surface composition of different elements were corrected with their corresponding atomic sensitivity factors using the Vision 2 software in Unix system.

2.3. Activity evaluation

The hydrogenolysis of CCl₂F₂ over the five different catalysts in this study was carried out in a fixed bed micro-reactor interfaced to a gas chromatograph equipped with an FID. The product mixture was injected into the GC column (Porapak-Q, 3 m long and 1/8" diameter made of S.S.) through a 6-port sampling valve after it is scrubbed with alkali (KOH solution) to remove the HCl/HF that evolve during the course of the reaction. The products were also analyzed and confirmed by GC–MS analysis. The earlier studies [2] showed the reaction temperature of 250 °C, a gas-hourly space velocity (GHSV) of 4000 h⁻¹ and a molar ratio of H₂/CCl₂F₂ of 8 as optimum reaction conditions over a 6 wt.% Pd supported on CMA-HT catalyst. Thus, the same conditions were chosen for the comparative study in the present work.

3. Results and discussion

3.1. BET-surface areas and acidities

Table 1 presents the BET-surface areas and acidities measured from TPD of NH₃ of the various fresh and used catalysts studied for the hydrodechlorination of CCl₂F₂. The surface areas of all the catalysts are found to be reduced after the reaction, which may be accounted for the transformation of the oxidic supports to their corresponding oxo/hydroxofluorides or fluorides [6,15]. Such transformation of alumina to its corresponding oxo/hydroxofluorides is also reported in the dismutation of CCl₂F₂ by Venugopal et al. [17] and Kemnitz et al. [18]. The acidities of the catalysts seemed to have en-

Table 1
BET-surface areas and acidities of fresh (calcined) and used supported Pd catalysts

Catalyst	BET-surface area (m ² g ⁻¹)		TPD of NH ₃ (μ mol m _{cat} ⁻²)	
	Fresh	Used	Fresh	Used
Pd/Al ₂ O ₃	152	92	0.97	1.98
Pd/CMA-HT	34	25	1.70	3.84
Pd/MgO	92	27	0.86	5.37
Pd/CMC-HT	46	24	0.13	0.13
Pd/Cr ₂ O ₃	95	52	–	–

hanced after the reaction again due to the same reason since the contribution of oxo/hydroxo fluorides or fluorides towards the increase in the Lewis acidity due to Mg^{2+} or Al^{3+} ions of the catalyst is higher compared to the O^{2-} ions. The increase in the acidity is higher in case of Pd/MgO and Pd/CMA-HT catalysts, which showed higher selectivity towards the formation of CH_2F_2 . Acidity of the support is one of the key factors that governs the selectivity of CH_2F_2 as shown by Coq et al. [5] in the hydrodechlorination of CCl_2F_2 over acidic supports like AlF_3 that acidic nature of the support facilitates an easier desorption of the intermediate $:\text{CF}_2$ from the electron deficient Pd species. The role of the support is to impart partial positive charge to Pd thus making it electron deficient ($\text{Pd}^{\delta+}$). In our earlier report [15], it is shown that increase in the acidity is higher over MgO than on Al_2O_3 after the reaction corresponding to the transformation of MgO to MgF_2 and Al_2O_3 to $\text{AlF}_{1.65}(\text{OH})_{1.35} \cdot x\text{H}_2\text{O}$ and a surface enrichment of fluoride being higher in case of MgO support (as observed from the TPD of NH_3 and XPS results). The higher selectivity of CH_2F_2 over MgO as compared to Al_2O_3 is attributed to this enhanced acidity. The selectivity towards CH_2F_2 over Pd/CMA-HT has been explained on similar grounds [2] but the higher selectivity to desired product here may also be due to a synergistic interaction of Pd with the support Mg–Al HT precursor probably to the ordered structure of the support and its precursor. In case of Pd/CMC-HT, there is no change seen in the acidity of the catalyst even after the reaction although the XRD patterns reveal the formation of MgF_2 and $\text{CrF}_3 \cdot 3\text{H}_2\text{O}$ phases. One reason may be that the support i.e., calcined Mg–Cr HT itself does not seem to have any considerable acidity/basicity [19] to have shown any enhancement in the acidity of this catalyst after the reaction.

3.2. XPS results

The XPS results (Table 2) clearly show the BEs of Pd $3d_{5/2}$ indicative of PdO in the calcined catalysts. Although presence of some metallic Pd species is observed in the XRD patterns, surface analysis by XPS has not revealed any such species. However, the used catalysts have clearly shown the presence of Pd^0 species with BEs ~ 335 eV along with the presence of some Pd peaks at 336–338 eV. These values have been ascribed [15] to the transformation of Pd^0 to Pd^+ or Pd^{2+} probably due to the presence of surface fluoride species. Shen et

al. [20] attributed the shift in the BE of Pd $3d_{5/2}$ from 335.1 to 336.2 eV in the Pd/MgO catalysts with Pd from PdCl_2 precursor to the intimate contact of Pd and Mg that lead to an electron transfer from Pd to Mg as evidenced by the presence of Pd^{n+} ions in reduced catalysts. The BE value of 51.2 eV in the Mg 2p spectra of the used catalyst of Pd/CMA-HT indicates the formation of MgF_2 from MgO of catalyst with Mg 2p BE of 49.8 eV. The BE value of Al 2p in reduced catalyst changed from 73.9 to 74.9 eV in used catalyst again indicates a partial transformation of Al_2O_3 to its oxo/hydroxo fluorides since the BE value of Al is intermittent to that present either in Al_2O_3 or AlF_3 (BE of Al 2p = 76 eV) [21]. The BEs of Cr 2p have been found to shift from 576.7 eV to 577.6 eV denoting the transformation of oxidic chromium to corresponding fluoride, which is also indicated in the XRD patterns of the used Pd/CMC-HT sample. The additional satellite peaks of Cr 2p are also observed in the Pd/CMC-HT samples at 578.6 and 579.5 eV in fresh and used catalysts, respectively, which is a characteristic phenomenon of the first row transition metal series. In fact, the transition metal ions have unfilled 3d orbitals [22,23] that show well separated satellite peaks in the core level XP spectra due to electron shake up and the structure of satellite reflects the nature of chemical bonding of the transition metal ions. Kemnitz et al. [24] in their extensive study of XPS on modified chromia catalysts for the chlorine/fluorine exchange reactions of CFCs showed the presence of strong secondary satellite structures on the high binding energy side in the Cr(III) 2p spectra. They reported the binding energy values of Cr $2p_{3/2}$ in $\alpha\text{-Cr}_2\text{O}_3$ and CrF_3 as 576.1 and 579.58 eV. A shift of the Cr $2p_{3/2}$ BE from 576.1 to 576.8 eV. The shift has been explained by a partial hydrogenation of surface chromium species. In another report Kemnitz et al. [18] have reported for the transformation of chromia to chromium hydroxyl fluoride which could only be seen in the samples containing >80% Cr in the dismutation of CCl_2F_2 over Cr and Mg containing catalysts. In the present report the shift of BE value of Cr 2p from 576.7 to 577.6 eV in Pd/CMC-HT catalyst can be attributed to the partial fluorination of surface chromium atoms. Although no oxo/hydroxo fluoride phases of chromium are found in the XRD analysis. Probably these phases may be present in X-ray amorphous form because of the lower Cr content in the Pd/CMC-HT catalyst. Kemnitz et al. [18] have observed the appearance of chromium hydroxofluoride phase only in the catalyst with

Table 2
Surface compositions of Pd, Mg, Al and F and their BEs from XPS analysis of fresh (calcined) and used supported Pd catalysts

Catalyst	Binding energies (eV)		Pd/M atomic ratio		F/M atomic ratio(used)
	Fresh	Used	Fresh	Used	
Pd/CMA-HT	Pd $3d_{5/2}$: 336.6; Mg 2p: 49.8; Al 2p: 73.9	Pd $3d_{5/2}$: 335.4, 336.7; Mg 2p: 51.2; Al 2p: 74.9; F 1s: 685.8	0.019	0.024	0.939
Pd/MgO	Pd $3d_{5/2}$: 336.9; Mg 2p: 49.8	Pd $3d_{5/2}$: 335.0; Mg 2p: 50.8	0.046	0.024	3.574
Pd/ $\gamma\text{-Al}_2\text{O}_3$	Pd $3d_{5/2}$: 337.2; Al 2p: 74.4	Pd $3d_{5/2}$: 334.9; Al 2p: 75.2; F 1s: 685.5	0.016	0.014	1.167
Pd/CMC-HT	Pd $3d_{5/2}$: 336.8; Mg 2p: 50.2; Cr 2p: 576.7, 578.6	Pd $3d_{5/2}$: 336.2, 338.2; Mg 2p: 51.7; Cr 2p: 577.6, 579.5; F 1s: 685.8	0.096	0.1287	1.349

M = Al or Mg or Al + Mg or Cr + Mg.

>80% Cr content. Similar observations can be made from the XPS spectra of Pd/MgO and Pd/Al₂O₃ catalysts which are discussed more in detail elsewhere [15]. The F/M (M = Al or Mg or Al + Mg or Cr + Mg) atomic ratios show the enrichment of fluorine on the surface of Pd/MgO and Pd/Al₂O₃ catalysts. The Pd/CMA-HT surface also shows the presence of fluorine but the ratio is not that high as in case of the other catalysts mentioned in Table 2. Pd/M (M = Al or Mg or Al + Mg or Cr + Mg) ratios indicate low amounts of Pd on the surface of the catalysts and it is interesting to note that there is not much variation in the surface composition of Pd even after the reaction on Pd/CMA-HT catalyst unlike the other catalysts which showed a considerable loss in the surface Pd content as seen from the Pd/M ratios of their used catalysts. In fact, there is a slight increase in the surface Pd content as observed from the increased Pd/M value in the used catalysts of Pd/CMA-HT and Pd/CMC-HT than in their fresh catalysts. This might be the probable reason for the higher stability of HT-precursor supported Pd catalysts over the other catalysts studied.

3.3. XRD results

Figs. 1 and 2 represent the X-ray diffraction patterns of calcined and used supported Pd catalysts, respectively, studied for the hydrodechlorination of CCl₂F₂. All the calcined catalysts showed the presence of very weak *d*-lines of α -Pd phase at $2\theta = 40^\circ$ for 2.25_x, $2\theta = 46.5^\circ$ for 1.95₄ and $2\theta = 67.9^\circ$ for 1.38₃ [ASTM no. 5-681] apart from the characteristic *d*-lines of their corresponding supports, viz., Cr₂O₃ [ASTM no. 6-504], γ -Al₂O₃ [ASTM no. 16-394], MgO [ASTM no. 4-829], poorly crystalline phase of MgO [ASTM no. 4-829] in case of calcined Mg–Al HT and Mg–Cr HT. The catalysts with HT-precursors as supports have shown the presence of HT-phase [ASTM no. 22-700] in case of Pd/CMA-HT and Stichtite phase [ASTM no. 14-330] in the XRD pattern of Pd/CMC-HT calcined catalyst. The presence of PdO phase [ASTM no. 6-515] is also indicated by the peaks with *d*-values: 2.64_x at 33.9°, 2.67₄ at 33.5° and 1.67₃ at 54.9° in the XRD patterns of all the calcined catalysts. The pattern of Cr₂O₃ supported catalyst showed some unidentified phases of chromium. The partial transformation of MgO to MgF₂ with *d*-values: 3.27_x at 27.2°, 2.23_x at 40.4° and 1.71₈ at 53.5° [ASTM no. 6-290], α -Pd to PdC_x with *d*-values: 2.303_x at 39.1°, 1.991 at 45.5° and 1.405 at 66.5° and γ -Al₂O₃ to AlF_{1.65}(OH)_{1.35}·*x*H₂O with *d*-values: 5.70_x at 15.5°, 2.98₅ at 29.9° and 1.74₃ at 52.6° [ASTM no. 18-24] is clearly evidenced in the XRD patterns of used catalysts. The calcined HTs also have transformed to corresponding fluorides or oxo/hydroxo fluorides with MgO–Al₂O₃ from Mg–Al HT to MgF₂ and AlF_{1.65}(OH)_{1.35}·*x*H₂O and MgO–Cr₂O₃ from Mg–Cr HT to MgF₂ and CrF₃·3H₂O with *d*-values: 4.70_x at 18.9°, 4.10₆ at 21.6° and 2.58₈ at 34.7° [ASTM no. 17-316], respectively. The transformation of oxidic supports to corresponding fluorides or oxo/hydroxofluorides is well known [6,15] in the hydrodechlorination of CFCs with the evolution of HCl/HF during the course of the reaction.

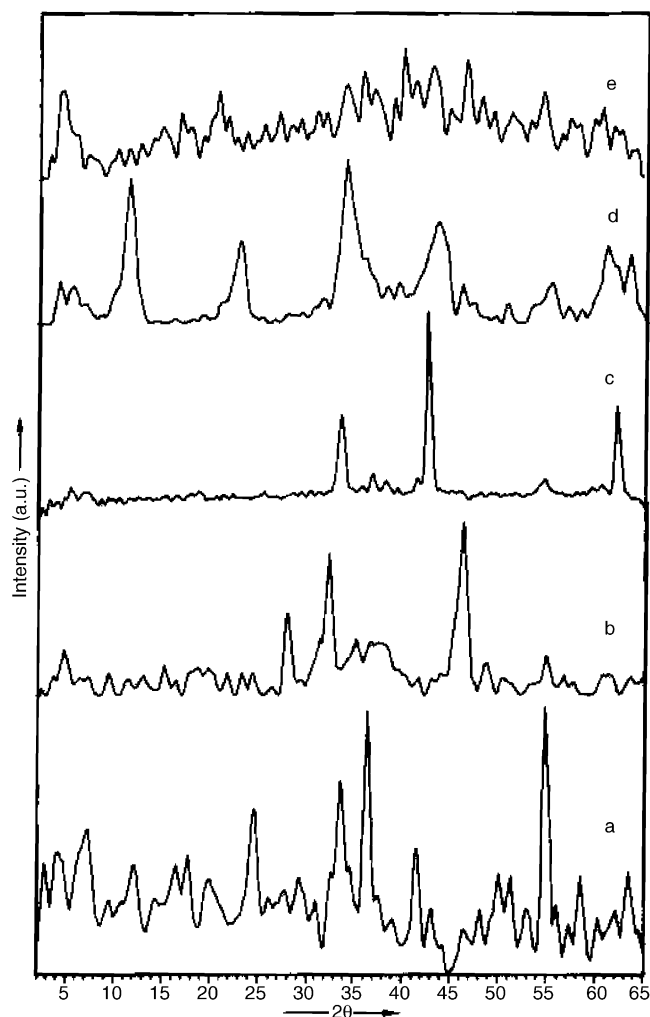


Fig. 1. X-ray diffraction patterns of calcined supported Pd catalysts. (a). Pd/Cr₂O₃, (b) Pd/ γ -Al₂O₃, (c) Pd/MgO, (d) Pd/CMA-HT, (e). Pd/CMC-HT.

3.4. TPR results

TPR profiles of the calcined and used supported Pd catalysts are presented in Figs. 3 and 4, respectively. Except for Pd/MgO and Pd/CMA-HT, all the other three catalysts have shown the presence of a negative signal at $\sim 90^\circ\text{C}$ corresponding to the decomposition of β -PdH_x that forms at slightly high temperature above ambient with the absorption of hydrogen into the sub-surfaces of metallic Pd [25,26] since, most of the palladium precursors are reported to reduce at ambient temperature itself in hydrogen atmosphere [27]. The appearance of a positive peak ~ 160 – 200°C in all the MgO containing catalysts, viz., Pd/MgO, Pd/CMA-HT and Pd/CMC-HT can be attributed to the delayed reduction of PdO species. Over Pd/MgO, the peak is observed at $\sim 160^\circ\text{C}$ which has been shifted to higher temperatures of 190 and 200°C in the CMA-HT and CMC-HT supported catalysts, respectively. The absence of β -PdH_x decomposition peak over Pd/MgO and Pd/CMA-HT may be attributed to the higher dispersion of Pd over these supports that may be obstruct-

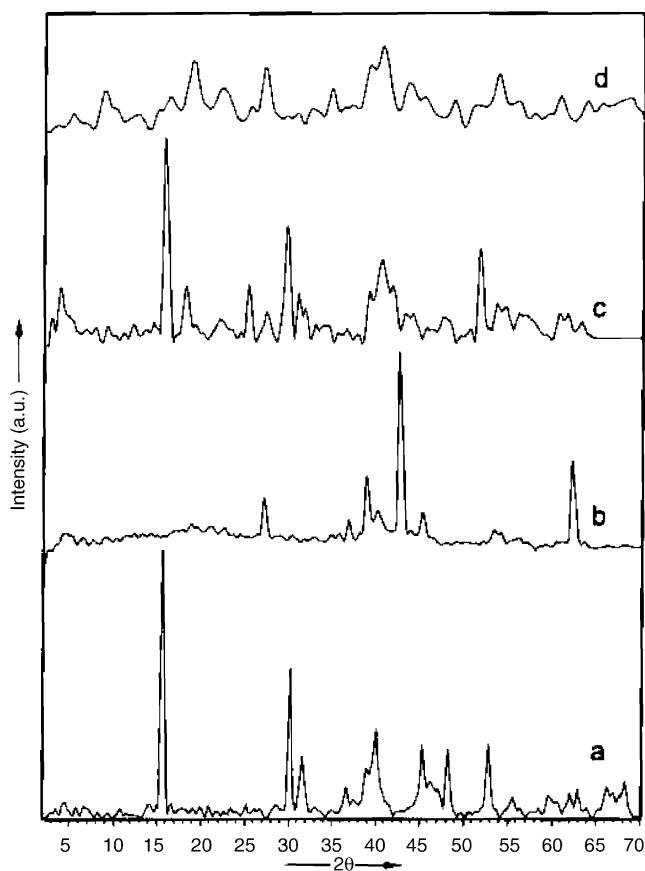


Fig. 2. X-ray diffraction patterns of used supported Pd catalysts. (a) Pd/ γ - Al_2O_3 , (b) Pd/MgO, (c) Pd/CMA-HT, (d) Pd/CMC-HT.

ing the absorption of hydrogen into sub-surfaces of Pd and thus the formation of any β -PdH_x and/or to the interaction of PdO and MgO delaying the reduction of PdO to form metallic Pd. The reduction peak of PdO in the TPR profiles of these catalysts also supports this assumption. The simultaneous negative and positive peaks at ~ 400 and above 500°C in the MgO containing catalysts may be ascribed to the partial desorption of hydrogen that is chemisorbed on both palladium and magnesia [28] and to the possible spill over of the hydrogen activated on metallic Pd to the support [29], respectively. The Pd/Cr₂O₃ catalyst showed two reduction maxima at 350 and 500°C corresponding to the loss of labile oxygen in two stages associated with Cr₂O₃ at high temperatures and a T_{max} at $\sim 650^\circ\text{C}$ which is also observed with Pd/CMC-HT probably to the bulk reduction of Cr₂O₃ [30].

The TPR patterns of all the used catalysts have shown the presence of β -PdH_x decomposition peak, which clearly indicates a transformation or reconstruction of Pd particles taking place during the course of reaction. The presence of β -PdH_x is an indication that Pd in the used catalysts is present majorly in metallic form. The other high temperature positive and negative signals at ~ 425 and $\sim 575^\circ\text{C}$ may be attributed to the consumption of hydrogen by carbonaceous species present on the catalyst surface and to the evolution of CH₄ (also confirmed by a coupled FID analysis of the outlet stream from

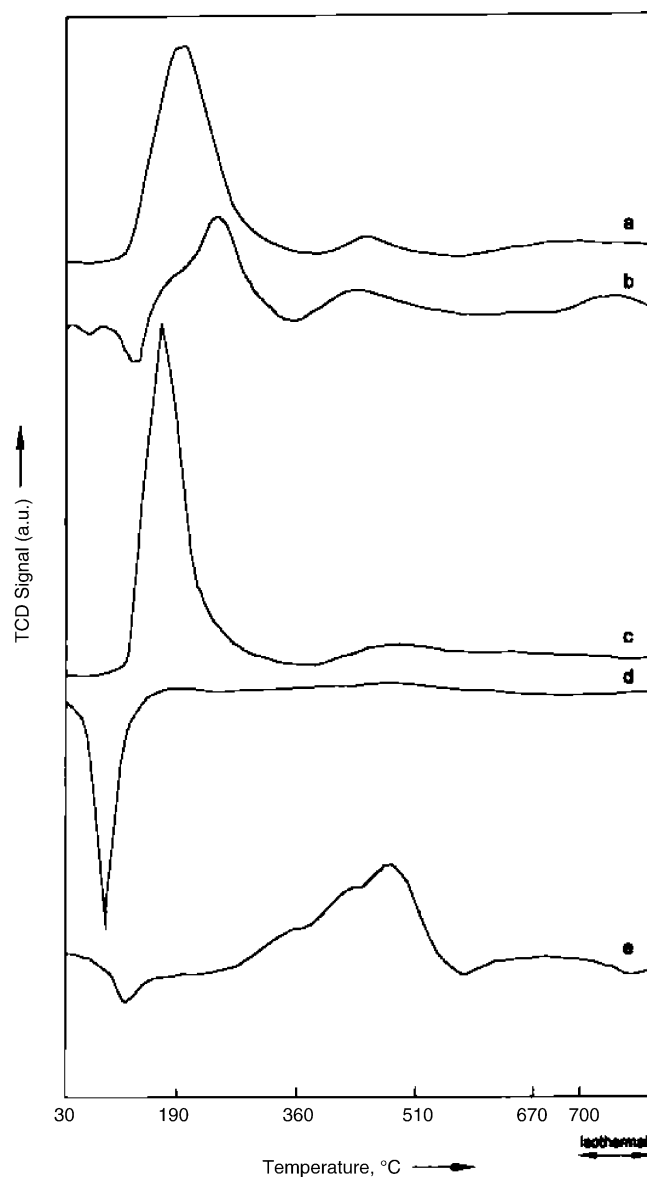


Fig. 3. TPR profiles of fresh (calcined) supported Pd catalysts. (a) Pd/CMA-HT, (b) Pd/CMC-HT, (c) Pd/MgO, (d) Pd/ γ - Al_2O_3 , (e) Pd/Cr₂O₃.

TCD) due to the reduction of coke moieties (CH_x, $x \geq 2$) present on the catalyst surface [1,15]. The presence of surface CH₂ species is also reported by Deshmukh and d'Itri [12] in the used Pd/AlF₃ catalyst.

3.5. Hydrodechlorination activity

The hydrodechlorination of CCl₂F₂ is studied over Pd supported on calcined Mg–Al HT and calcined Mg–Cr HT catalysts and their activities have been compared to the activities of their individual single supported Pd catalysts namely Pd/MgO, Pd/ γ - Al_2O_3 and Pd/Cr₂O₃. Our earlier studies [1,2] have demonstrated that the supports from the HT-precursors to be highly active for this reaction. The optimized reaction conditions in those studies with a reaction temperature of

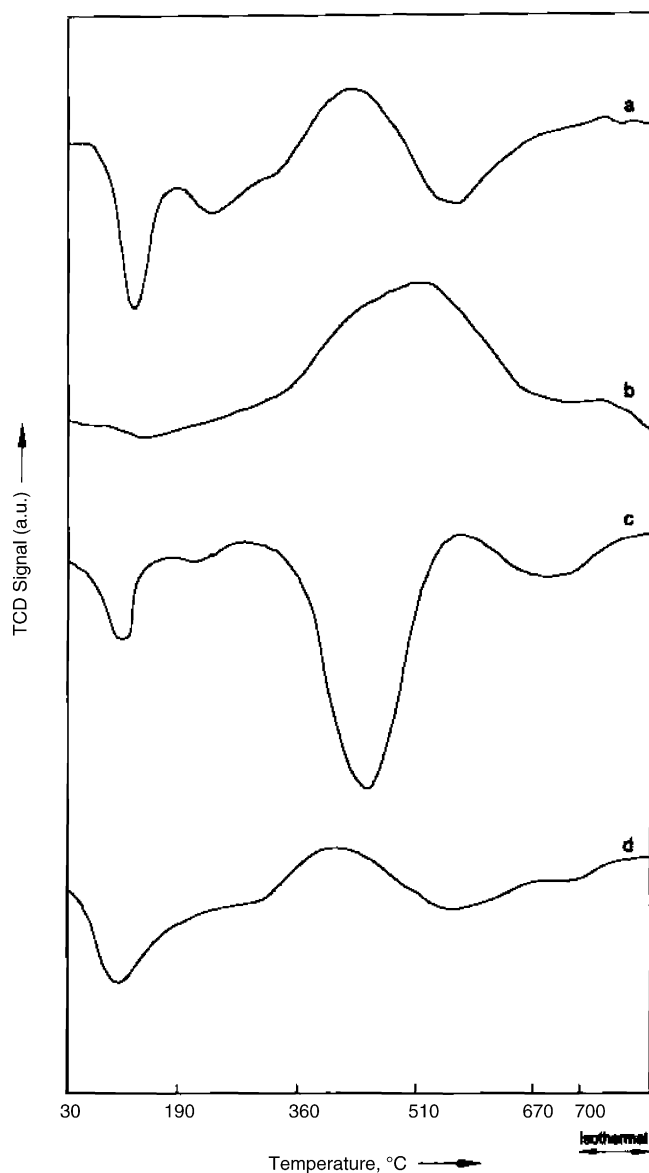


Fig. 4. TPR profiles of used supported Pd catalysts. (a) Pd/CMA-HT, (b) Pd/CMC-HT, (c) Pd/MgO, (d) Pd/ γ -Al₂O₃.

250 °C, GHSV = 4000 h⁻¹ and H₂/CCl₂F₂ molar ratio of 8 are taken as the standard conditions in the present work for screening the catalysts. Fig. 5 shows the time-on-stream activities of the various catalysts studied, which clearly indicates that a steady state is reached in about 4–5 h of the reaction. Hence, the activity data at 6 h is taken as a steady state activity. An increasing trend in the % conversion of CCl₂F₂, % selectivity to CH₂F₂ (correspondingly the % yield of CH₂F₂) and a decreasing trend in the % selectivity to CH₄ are observed in all most all the catalysts except for Mg–Cr HT, which showed an increased selectivity towards CH₄ with time.

Table 3 depicts the comparative steady state activities of catalysts studied for the hydrodechlorination of CCl₂F₂. The table reveals the advantage of HT-precursor especially

Mg–Al HT in the selective synthesis of CH₂F₂ from CCl₂F₂ over the other catalysts. The selectivity towards CH₂F₂ over these catalysts are observed in the order: Pd/CMA-HT > Pd/MgO > Pd/ γ -Al₂O₃ > Pd/Cr₂O₃ > Pd/CMC-HT. The higher hydrogenolytic activity of Pd/MgO catalyst in complete cleavage of C–Cl bonds has been ascribed to the strong hydridic character of hydrogen atoms chemisorbed on the electron-rich Pd particles in strong contact with O²⁻ sites of MgO [31,32]. Also, MgO support is reported to adsorb chlorine [33] thus facilitating easier cleavage of C–Cl bonds. But no chloride compounds of magnesium are detected either from XRD or XPS analyses though Choi et al. [34] reported for the formation of MgCl₂·xH₂O phase after the reaction in the hydrodechlorination of CCl₄. Thus MgO seem to play an important role in removing Cl from the reactant molecule and thus facilitating the easier formation of the desired product. The absence of any magnesium chloride may be that the Cl that is adsorbed by MgO must be scavenging off in the form of HCl during the course of the reaction.

The selectivity to CH₂F₂ is known to be governed mainly by the particle size or dispersion, geometry of the Pd crystallites and the nature of the support i.e., acidity of the support [5]. Juszczak et al. [11] have shown that bulky Pd particles constitute a more capacious sink for carbon and contain higher proportion of surface plane sites. Further, they suggested carbided Pd surfaces to be the sites of high selectivity towards CH₂F₂. According to Coq et al. [5], the Lewis acidity of the supports like AlF₃ enhances the electron deficiency of Pd facilitating the easier desorption of the surface intermediate :CF₂ species, which are responsible for the higher selectivity to CH₂F₂. They have clearly demonstrated in the mechanism proposed for the hydrodechlorination of CCl₂F₂ that the desorption of :CF₂ intermediate is the rate-governing step. If :CF₂ species resides for a longer time on Pd surfaces, defluorination is favored leading to the formation of CH₄ in more amounts. Thus, the enhanced acidities of the catalysts (after the reaction) in Pd/CMA-HT and Pd/MgO with the transformation of the oxidic supports (MgO–Al₂O₃ and MgO) to corresponding fluorides or hydroxofluorides (MgF₂, AlF_{1.65}(OH)_{1.35}·xH₂O and MgF₂) as evidenced clearly from XRD patterns and from the surface analysis by XPS of the catalysts explains the higher selectivity of CH₂F₂ over these catalysts. And it seems that the lack of sufficient acidity on Pd/CMC-HT is the reason for the higher formation of CH₄. As there is no driving force for the easier desorption of :CF₂ from Pd species (i.e., the electron deficiency factor of Pd as in Pd/CMA-HT or Pd/MgO), higher selectivity to CH₄ over this catalyst is favored. This also indicates the dominative role of the acidity of the catalyst over the other main factor i.e., particle size of Pd. The TPR patterns clearly show the presence of β -PdH_x species for which larger Pd particles are required, because formation of β -PdH_x is a bulk phenomenon. XRD results also show the presence of larger particles of Pd. Thus larger Pd particles may be one of the reason for getting higher yield of CH₂F₂.

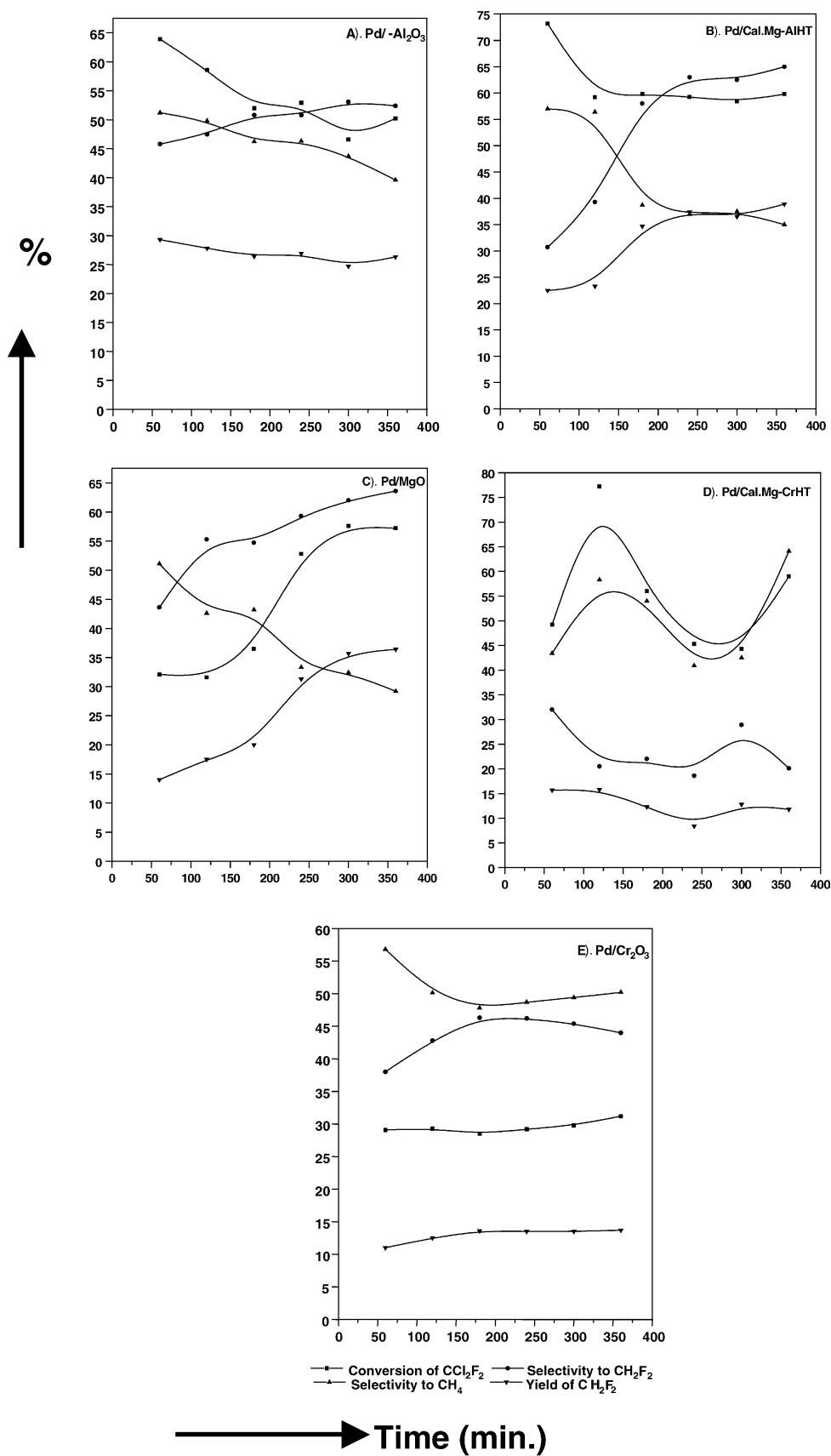


Fig. 5. Time-on-stream activity of supported Pd catalysts in the hydrodechlorination of CCl₂F₂.

Table 3
Steady-state activities of different supported Pd catalysts in the hydrodechlorination of CCl_2F_2

Catalyst	% Conversion of CCl_2F_2	% Selectivities ^a of		% Yield of CH_2F_2
		CH_2F_2	CH_4	
Pd/ Al_2O_3	50.2	52.4	39.6	26.3
Pd/CMA-HT	60	65	35	39.0
Pd/MgO	57.2	63.6	29.2	36.4
Pd/CMC-HT	59	20.1	64.1	11.8
Pd/ Cr_2O_3	31.2	44	50.2	13.6

^a Remaining % selectivity corresponds to other products, viz., CHClF_2 and CHF_3 .

The report by Shen et al. [20] shows the strong ability of chlorine anions to stabilize the bridge structure of Pd (Cl, Cl) Mg^{2+} and to transfer electrons from Pd to Mg^{2+} in the catalysts with Cl-containing Pd precursors, which has been evidenced by the presence of Pd^{n+} ions in reduced catalysts. Thus, the BE of Pd $3d_{5/2}$ ~ 336.2 eV in the Pd/MgO and Pd/CMA-HT catalysts may be attributed to the intimate contact of Pd and Mg^{2+} leading to the electron transfer from Pd to Mg as attributed by Shen et al. [20] from their XPS studies. This can also explain the higher selectivity to CH_2F_2 formation over these catalysts with electron deficiency generated on Pd by this contact.

The activity study over Pd/CMA-HT and Pd/MgO has clearly established the superiority of Pd/CMA-HT in terms of the stability showing a very stable and almost same activity even after 30 h time on stream where as Pd/MgO although showed good selectivity to CH_2F_2 , suffered loss in activity after about 15 h showing about 35–40% conversion of CCl_2F_2 . However, the selectivity to CH_2F_2 over Pd/MgO has not varied much even after 15 h time on stream. The other catalysts, viz., Pd/ Al_2O_3 and Pd/ Cr_2O_3 also showed loss in activity after 10 h itself. The Pd/CMC-HT even though showed stable activity, it is only found to be more selective for CH_4 formation than for CH_2F_2 . The Pd/(Al + Mg) surface ratio obtained from XPS analysis showed not much change even after the reaction, which may be taken as one of the reasons for it to show a very stable activity. The higher activity and selectivity of Pd/CMA-HT may be attributed to a synergistic interaction of Pd and the support components in calcined Mg–Al HT.

4. Conclusions

1. The Hydrodechlorination activity performance of the catalysts is found to be in the order: Pd/CMA-HT > Pd/MgO > Pd/ Al_2O_3 > Pd/ Cr_2O_3 > Pd/CMC-HT.
2. β -PdH_x decomposition peak is absent in the TPR patterns of Pd/MgO and Pd/CMA-HT fresh catalysts corresponding to delay in PdO reduction (shifting of T_{max} towards the high temperature) due to higher dispersion or the interaction between PdO and MgO. Presence of PdO is observed in the XRD patterns of these catalysts.
3. Transformation of oxidic supports into fluorides/hydroxofluorides as evidenced from both the XPS and XRD analysis and also the enhanced acidities observed

by TPD of NH_3 of used catalysts compared to fresh catalysts; manifested the higher selectivities towards CH_2F_2 over Pd/CMA-HT and on Pd/MgO compared to other catalyst systems.

4. Pd/CMC-HT showed a deeper hydrogenation activity towards the formation of CH_4 , which is presumably due to the poor acidity of the catalyst compared to other systems.
5. The higher stability of Pd/CMA-HT can be observed from the absence of any change in the surface Pd composition in the XPS analysis and the synergistic interaction of Pd with the support, calcined Mg–Al HT.

Acknowledgments

The authors thank Dr. J.S. Yadav, Director, Indian Institute of Chemical Technology, Hyderabad, India for his keen interest in this work and permitting to publish these results. The authors, AHP and VSK thank the Council of Scientific and Industrial Research, New Delhi, India for the award of fellowships.

References

- [1] A.H. Padmasri, A. Venugopal, J. Krishnamurthy, K.S. Rama Rao, P. Kanta Rao, J. Mol. Catal. A 181 (2002) 73.
- [2] A.H. Padmasri, A. Venugopal, B. Sreedhar, P. Kanta Rao, K.S. Rama Rao, M.S. Scurrell, in communication.
- [3] A. Morato, C. Alonso, F. Medina, Y. Cesteros, P. Salagre, J.E. Sueiras, D. Tichit, B. Coq, Appl. Catal. B: Environ. 32 (2001) 167.
- [4] R. Ohinishi, R. Wang, W.-L. Wang, M. Ichikawa, Chem. Lett. (1991) 841.
- [5] B. Coq, J.M. Cognion, S. Hub, F. Figueras, D. Tournignant, J. Catal. 141 (1993) 41.
- [6] B. Coq, F. Figueras, S. Hub, D. Tournignant, J. Phys. Chem. 99 (1995) 159.
- [7] Z. Karpinski, K. Early, J.L. d'Itri, J. Catal. 164 (1996) 378.
- [8] A. Wiersma, E.J.A.X. van de Sandt, M. Makkee, H. van Bekkum, J.A. Moulijn, Stud. Surf. Sci. Catal. 101 (1996) 369.
- [9] B.S. Ahn, S.C. Lee, D.J. Moon, B.G. Lee, J. Mol. Catal. A 106 (1996) 83.
- [10] A. Wiersma, E.J.A.X. van de Sandt, M.A. den Hollander, H. van Bekkum, M. Makkee, J.A. Moulijn, J. Catal. 177 (1998) 29.
- [11] W. Juszczycy, A. Malinowski, Z. Karpinski, Appl. Catal. A: Gen. 166 (1998) 311.
- [12] S. Deshmukh, J.L. d'Itri, Catal. Today 40 (1998) 377.
- [13] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, J.A. Moulijn, Appl. Catal. A: Gen. 173 (1998) 352.

- [14] A. Malinowski, W. Juszczak, J. Pielaszek, M. Bonarowska, M. Wojciechowska, Z. Karpinski, *J. Chem. Soc., Chem. Commun.* 8 (1999) 685.
- [15] A.H. Padmasri, A. Venugopal, J. Krishnamurthy, K.S. Rama Rao, P. Kanta Rao, G. Kishan, J.W. Niemantsverdriet, *J. Phys. Chem. B* 106 (2002) 1024.
- [16] W.T. Reichle, *J. Catal.* 94 (1985) 547.
- [17] A. Venugopal, K.S. Rama Rao, P.S. Sai Prasad, P. Kanta Rao, *J. Chem. Soc., Chem. Commun.* (1995) 2377.
- [18] E. Kemnitz, A. Hess, G. Rother, S. Troyanov, *J. Catal.* 159 (1996) 332.
- [19] A.H. Padmasri, A. Venugopal, V. Durga Kumari, K.S. Rama Rao, P. Kanta Rao, *J. Mol. Catal. A* 188 (2002) 255.
- [20] Y. Shen, S. Wang, K. Huang, *Appl. Catal. A: Gen.* 57 (1990) 55.
- [21] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of XPS*, Perkin-Elmer, Eden Prairie, MN, 1992.
- [22] D.C. Frost, A. Ishitani, C.A. Mc Davell, *Mol. Phys.* 24 (1972) 861.
- [23] T.A. Carlson, *Photoelectron and Auger spectroscopy*, Plenum Press, New York, 1975.
- [24] E. Kemnitz, A. Kohne, I. Grohmann, A. Lippitz, W.E.S. Unger, *J. Catal.* 159 (1996) 270.
- [25] M. Lagos, *Surf. Sci. Lett.* 122 (1982) 601.
- [26] G. Fagherazzi, A. Beneditti, S. Polizzi, A. Di Mario, F. Pinna, M. Signoretto, N. Pernicone, *Catal. Lett.* 32 (1995) 293.
- [27] A.W. Stobbe-Kreemers, M. Soede, M. Makkee, J.J.F. Scholten, *Appl. Catal. A: Gen.* 131 (1995) 293.
- [28] Y.Z. Chen, C.M. Hwang, C.W. Liaw, *Appl. Catal. A: Gen.* 169 (1998) 207.
- [29] T. Itoh, M. Kuramoto, M. Yoshida, T. Tokuda, *J. Phys. Chem.* 87 (1983) 4411.
- [30] H.E. Curry-Hyde, H. Musch, A. Baiker, M. Schraml-Marth, A. Wokaun, *J. Catal.* 133 (1992) 397.
- [31] V. Dal Santo, L. Sordelli, C. Dossi, S. Recchia, E. Fonda, G. Vlaic, R. Psaro, *J. Catal.* 198 (2001) 296.
- [32] M. Kappers, C. Dossi, R. Psaro, S. Recchia, A. Fusi, *Catal. Lett.* 39 (1996) 183.
- [33] V. Dal Santo, C. Dossi, S. Recchia, P.E. Colavita, G. Vlaic, R. Psaro, *J. Mol. Catal. A* 182 (2002) 157.
- [34] H.C. Choi, S.H. Choi, O.B. Yang, J.S. Lee, K.H. Lee, S.Y. Kim, *J. Catal.* 161 (1996) 790.