



Selective hydrogenolysis of dichlorodifluoromethane (CCl_2F_2) over CCA supported palladium bimetallic catalysts

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Abstract

La, Bi, Sb, Sn, Ba, and Zn are chosen for addition on carbon covered alumina (CCA) supported Pd catalyst. The effect of these second metals on supported Pd catalysts has been studied for the hydrogenolysis activity of CCl_2F_2 . Bi and Sb promoters have been found to improve not only the thermal stability but also selectivity towards CH_2F_2 . Sn bimetallic catalyst exhibited high selectivity towards CHClF_2 . This may be explained on the basis of the metal–metal interactions that influence the reducibility of the palladium. These improved properties arise due to inter-metallic compound formation as evidenced from the XRD and TPR data on CCA supported bimetallic palladium catalysts. The effect of addition of second metal on Pd/CCA catalyst is screened in terms of partial dehalogenation ability and thermal stability for hydrodechlorination activity of CCl_2F_2 to maximize the CH_2F_2 yield.

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1. Introduction

Bimetallic catalysts are increasingly used in place of monometallic catalysts to catalyze numerous reactions because of their unique properties. There are several advantages like, (i) higher catalyst life times (ii) improved selectivity and activity compared to those of monometallic catalysts. Considerable amount of literature is available on bimetallic catalysts for various applications from reforming to automobile emission control [1–5]. The performance of a catalyst is governed by its aging/thermal resistance and it is observed that in supported metal catalysts, the catalyst may be

affected by coking, poisoning and moreover in presence of hydrogen most of the noble metal catalysts undergo sintering during the course of reaction [1–5]. Several literature reports reveal that addition of a second metal to the catalyst may prevent sintering there by reducing deactivation that occurs in monometallic catalysts.

Coq and Figueras have studied the influence of Co-metal on Pd based catalysts in hydrodearomatization, hydrogenation of nitrogen containing compounds reaction involving CO, etc. The authors opined that no specific interpretation to explain the effect of Co-metal on the performance of Pd catalysts and it depends on the nature of both the Co-metal and the type of reaction [6]. In many cases the promotion of the catalytic properties will be directly related to the method

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of preparation and how it effects chemical state of Pd and Co-metal [6]. Some of these studies [7–11] indicate that the second metal modifies the catalytic properties by forming an inter-metallic or alloy compound with Pd there by altering the selectivity of the catalyst. Few reports available on C–Cl hydrogenolysis, which deal with bimetallic catalysts on conventional supported systems like alumina and carbon [7–11].

Conversion of (CCl_2F_2) CFC-12 to (CH_2F_2) HFC-32 assumes importance as because HFC-32 is identified as a deep refrigerant [12].

In our recent study, carbon covered alumina (CCA) supported Pd catalyst shown good hydrodechlorination activity, the thermal stability of this catalyst at and above 260°C reaction temperature is poor and sintering is found to be one of the major reasons for deactivation of the catalyst [13]. Present study deals with the CCA supported bimetallic palladium catalysts on thermal stability and product selectivity aspects in the hydrodechlorination of CCl_2F_2 .

2. Experimental

Supported palladium bimetallic catalysts were prepared by taking different metal salts using carbon covered alumina (CCA) as support. The preparation of support was described elsewhere [13]. The requisite amount of PdCl_2 (Aldrich, AR grade, USA >99%) was dissolved in dilute aqueous hydrochloric acid solution to get 0.134 g Pd/ml solution. SnCl_2 , SbCl_3 , ZnCl_2 and $\text{La}(\text{NO}_3)_3$, $\text{Bi}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$ (Aldrich AR Grade, assay >98%) were employed to prepare the bimetallic catalysts. The bimetallic catalysts were prepared by co-impregnation of requisite amounts of respective aqueous solutions of the two metal salts on CCA support to get a M/Pd (M is second metal) atomic ratio of 0.5, by following the conventional wet impregnation (excess solvent) technique [14]. In all the bimetallic catalysts, Pd loading was maintained at 4% by weight, which is found to be optimum in our earlier study [13]. After evaporating the excess solvent on a water bath, the catalyst mass was dried in an oven at a temperature of 120°C for 12 h. The catalysts were designated as SnCCA, SbCCA, ZnCCA, LaCCA, BiCCA and BaCCA. The oven dried catalyst samples were directly used for the activity experiments and in situ reduction (at 400°C for 4 h) was performed prior to the activity

experiments under hydrogen atmosphere. Some part of the oven dried catalyst sample was subjected to reduction in hydrogen at 400°C for 4 h and passivated in nitrogen atmosphere. These reduced samples were used for X-ray diffraction analysis.

The catalysts were characterized by BET surface area, XRD and TPR techniques. Powder X-ray diffraction patterns of the catalysts were recorded with a Siemens D-5000 X-ray diffractometer using $\text{Cu K}\alpha$ radiation. BET surface areas were determined by nitrogen adsorption at -196°C using an all glass high vacuum system. Temperature programmed reduction (TPR) of the catalysts (100–150 mg) were performed using a 6% H_2 –94% Ar gas mixture at a heating rate of $11^\circ\text{C}/\text{min}$ with a gas flow rate of 20 ml/min. During the TPR experiments differential conductivity also recorded along with TPR. The experimental procedure was explained in our earlier communication [13].

Hydrodechlorination of CCl_2F_2 was carried out in a micro reactor inter-faced on-line with a gas chromatograph equipped with a FID. Acid free product mixture was analyzed at regular time intervals. The CCl_2F_2 and hydrogen were mixed in a molar ratio 1:8 and passed over the catalyst bed (approximately 1.0 g) at a space velocity of 4800 h^{-1} [13]. The reaction was carried out at reaction temperatures ranging between 200 and 320°C , after reducing the dried catalyst in H_2 at 400°C for 4 h. The major components of the product mixture are CH_2F_2 , CH_4 and CCl_2F_2 ; minor components are CHClF_2 and CHF_3 depending up on the reaction conditions and employed catalyst.

3. Results and discussions

The XRD patterns of bimetallic Pd catalysts, reduced and used, are given in Fig. 1A and B, respectively. In all the reduced catalysts, some amount of Pd is interacted with the second metal and free Pd (α -Pd) can also be observed from corresponding XRD patterns. Because of the close proximity of reflections of the interacted phases and α -Pd, it is difficult to distinguish the corresponding inter-metallic phases from the condensed XRD patterns. However, one can clearly observe the shifting of XRD signals in bimetallic catalysts compared to that of monometallic catalysts.

BET surface areas of reduced catalysts and major phases identified from XRD patterns of reduced and

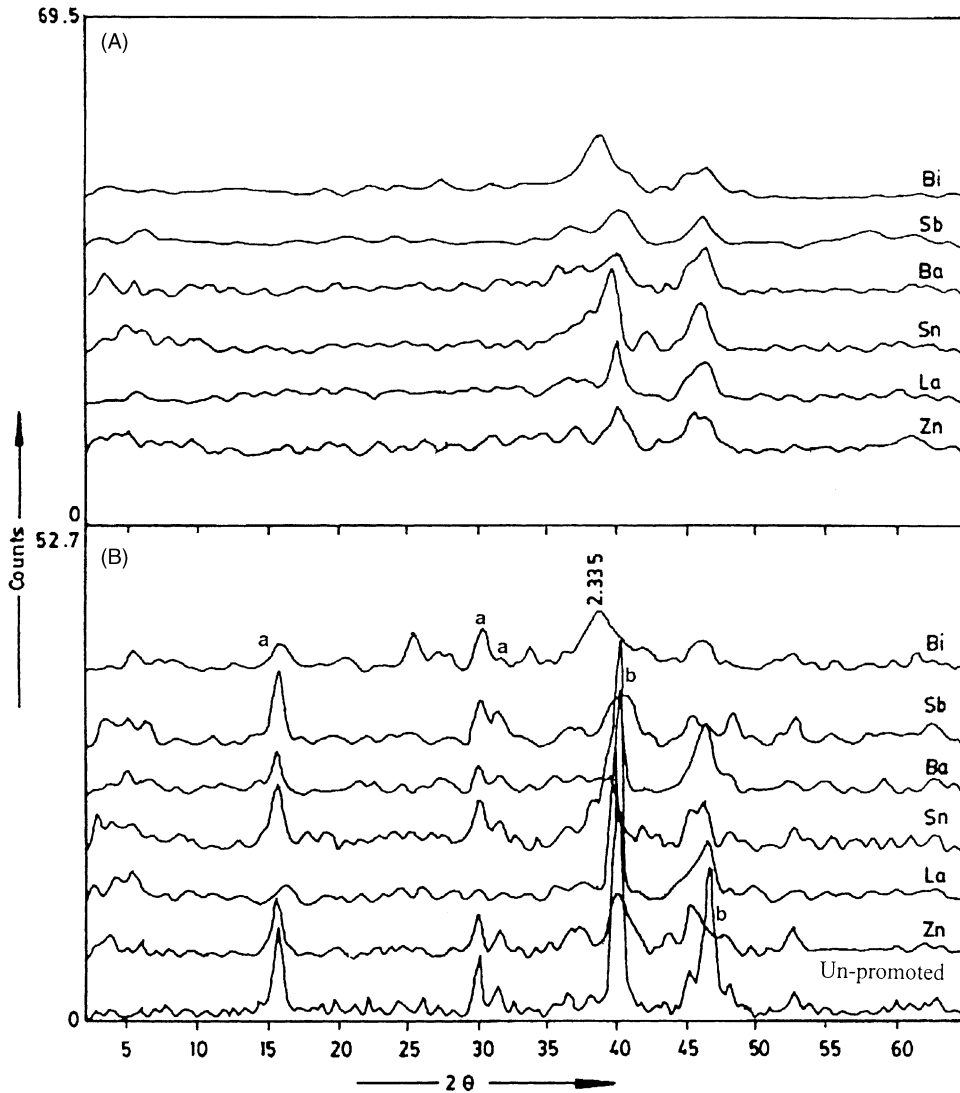


Fig. 1. XRD patterns of bimetallic Pd/CCA catalysts: (A) reduced catalysts; (B) used catalysts (Pd wt.% = 4 and M/Pd = 0.5 atomic ratio). (a) $\text{AlF}_{1.96}(\text{OH})_{1.04}$, (b) α -Pd.

used bimetallic catalysts are given in Table 1. No Pd inter-metallic phases or interacted Pd species are observed in BaCCA fresh and used catalysts. The reflections with weak signals of α -Pd can be seen in all the reduced catalysts except SbCCA catalyst. In used catalysts in addition to the interactive Pd some inter-metallic phases and aluminum hydroxide fluoride ($\text{AlF}_{1.9}(\text{OH})_{1.04}$; d values of 5.56, 2.9, 2.78, ASTM 11-631) can also be seen and this is attributed to the reaction of HF with uncovered alumina surface

during the course of reaction. Even though most of the alumina covered by carbon during the support synthesis still some of the alumina sites are available to access for HF [13].

It is interesting to observe the reflections of $(\text{Bi}_3\text{Pd})_{16}\text{O}$ (2.35, 2.20, 2.41, ASTM 23-851) as a major phase in both reduced and used BiCCA catalyst. Presence of oxygen in this phase even under reductions conditions it seems quite possible as $\text{Bi}(\text{NO}_3)_3$ decomposed to corresponding oxide and the Bi_2O_3

Table 1
XRD data of CCA supported palladium bimetallic catalysts

Catalyst	BET-SA (m ² g ⁻¹)	XRD phases		ASTM no.
		Reduced	Used	
Pd/CCA	131	α -Pd	α -Pd ^a	
SnCCA	103	α -Pd ^a ; Pd ₃ SnC _{0.5} ^b	α -Pd ^a ; Pd ₃ SnC _{0.5} ^b	28-723
ZnCCA	97	α -Pd ^a ; Pd ₅ Zn ₂₁ ^c	PdZn ₂ ^a	34-1215
LaCCA	84	Pd ₃ La; α -Pd	α -Pd ^a ; Pd ₃ La ^c	17-67
BaCCA	118	α -Pd ^a	α -Pd ^a	
SbCCA	91	Pd _x Sb _y	Pd _x Sb _y	23-36, 597
BiCCA	110	(Bi ₃ Pd)16O ^a ; α -Pd ^c	α -Pd ^c ; (Bi ₃ Pd)16O ^a	23-851

M/Pd atomic ratio = 0.5 and Pd wt.% = 4.

^a Major.

^b Medium.

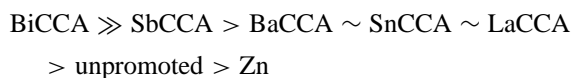
^c Low intensities.

may not be completely reducing under employed conditions. More over oxygen in this phase appears to have been added as the catalyst samples were exposed to air after reaction/reduction. However, the XRD data reveal that the entire Pd is not free from the second metal and a number of inter-metallic compounds have been observed and their intensities are quite different from each other implying that the metallic radii of the second metal and its valence electrons are responsible for the degree of metal–metal interactions observed in the corresponding XRD patterns. However, as Ponc described the important aspects of bimetallic catalysts based on the mixing enthalpy change its size and sign (either positive or negative). When the mixing enthalpy of the bimetallic system is large and negative should form inter-metallic compounds [15].

The TPR patterns of bimetallic Pd/CCA fresh catalysts are represented in Fig. 2. The TPR results reveal that catalyst reduction is taking place in multi-stages. The Ba, Sn and Zn bimetallic CCA fresh catalysts have exhibited a broad negative peak corresponding to the decomposition of β -PdH_x. Presence of this peak may give an indication that free Pd is available in these catalysts. On the other hand, La, Sb and Bi bimetallic catalysts have not exhibited any hydride decomposition peak, implying that most of the Pd is in dispersed state or in an interacted form [6].

The second reduction peak centered between 300 and 500 °C, which indicates high hydrogen consumption is associated with these bimetallic catalysts. High hydrogen consumption revealed by TPR is mainly due to three factors: (i) spill-over hydrogen due to the pres-

ence of carbon moiety in CCA (ii) chloride reduction (i.e. stabilized chloride on support, which reacts with spill-over hydrogen to form HCl) [13] (iii) some of the second metal is reduced at a low temperature assisted by Pd to form a corresponding inter-metallic phase [10]. It is interesting to observe that the T_{max} of this peak is shifted to a higher temperature compared to that of the monometallic catalyst. The intensities of this peak are in the following order:



A broad peak with a shoulder (>550 °C smaller in intensity) is ascribed to the hydrogen uptake in bulk carbon reduction. At high temperature, the negative peak centered at ~700 °C is attributed to the reduction (reaction of carbon with H₂) of coke deposited on alumina (which is deposited during the pyrolysis) evolved as hydrocarbons. TPR patterns of used catalysts (Fig. 3) indicate that LaCCA, BaCCA and BiCCA bimetallic catalysts show a broad negative peak centered between 90 and 120 °C. This is attributed to the evolution of H₂ from the decomposition of β -PdH_x indicating that considerable amount of Pd is present in free form. XRD patterns of Ba promoted catalyst indicate the absence of Pd-Ba inter-metallic compound. Addition of second metal may be preventing the sintering of Pd as expected; however, some of the Pd particles might have become free during the reaction or reduction at 400 °C for 4 h. Reorganization of Pd appears to be taking place leading to the

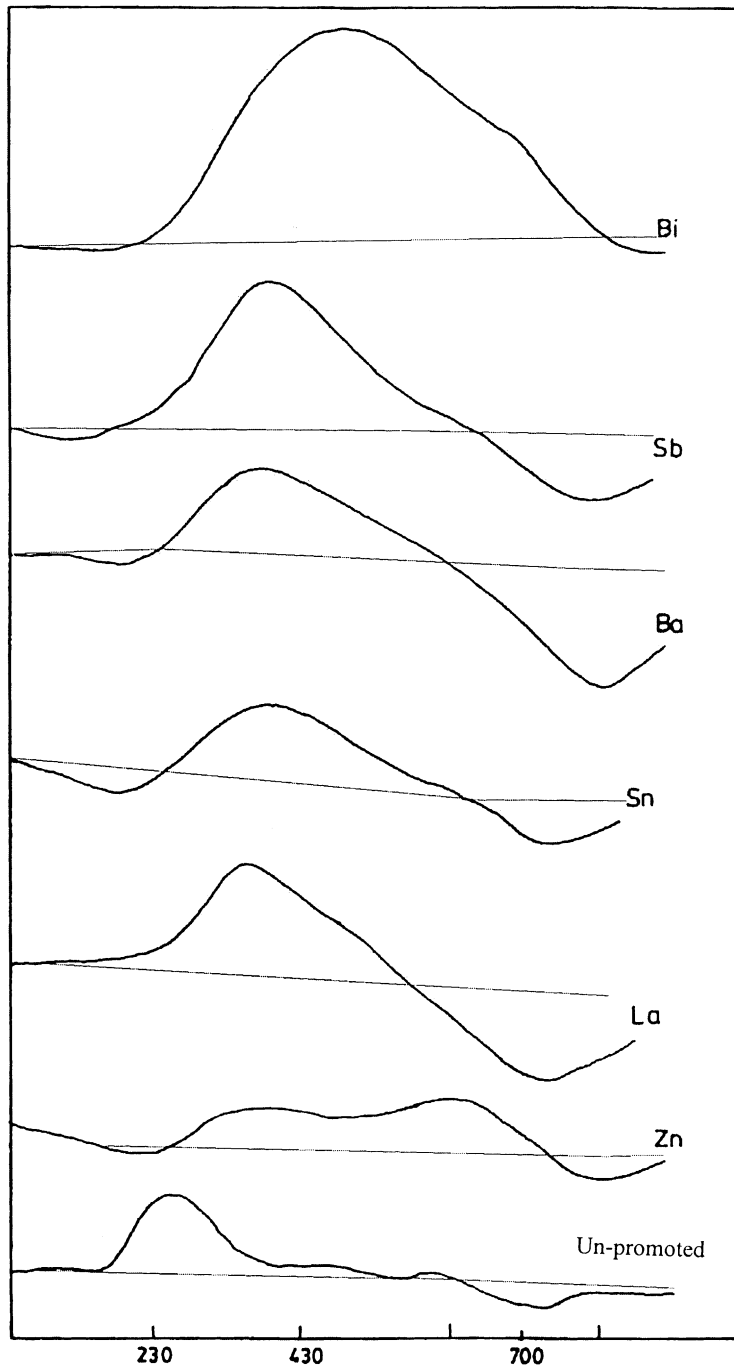


Fig. 2. TPR patterns of bimetallic Pd/CCA fresh catalysts.

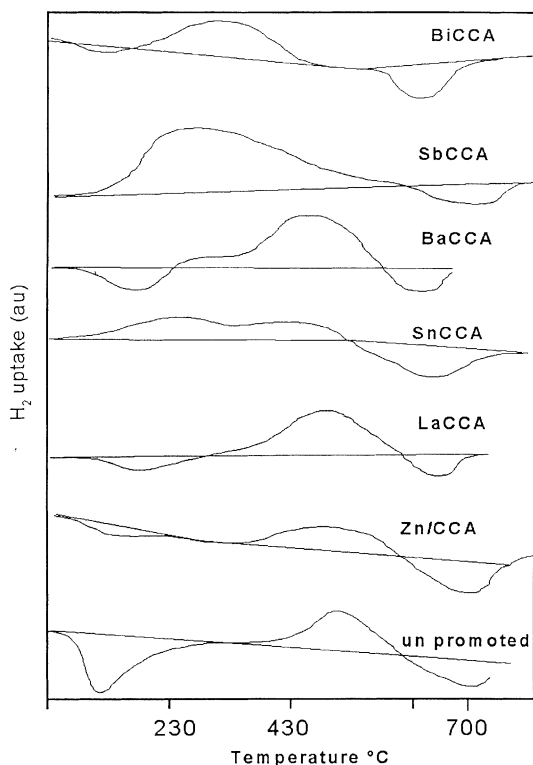


Fig. 3. TPR patterns of bimetallic Pd/CCA used catalysts.

formation of larger crystallites, which is responsible for the formation of the β -PdH_x phase that appeared in its reduction pattern. This phenomenon is not observed in used Sb, Sn and Zn bimetallic catalysts indicating that Pd particles may not be sufficiently big warranting the formation of β -PdH_x. However, in all bimetallic catalysts the intensity of β -PdH_x decreased due to the alloy have expanded lattices compared to the Pd [6,16].

Peak centered between 200 and 450 °C is observed in SbCCA and BiCCA catalysts and is absent in all the remaining bimetallic catalysts. In other catalysts, reduction peaks are present at higher temperatures. These peaks may be attributed not only to the reduction of carbon but also perhaps to the reduction of the MO_x to form an inter-metallic phases with Pd. ZnCCA and SnCCA bimetallic catalysts exhibited two broad reduction peaks with very low intensities. It is clear from their XRD data that most of the Pd is associated with Sn as Pd₃SnC_{0.5} and in Zn, as PdZn₂. Even though the Pd–Sn phase is of minor intensity (from its XRD) the stoichiometry is 3 with respect to the Zn.

Thus, most of the Pd might have contributed to form this Pd–Sn carbide phase. Presence of carbon in this phase as support consists of sufficient carbon, which might have dissolved during the course of reduction [17,18].

It is interesting to observe that the peaks centered at 250–300 °C are associated with high hydrogen consumption with high peak intensity in SbCCA used catalyst comparable to those of BiCCA catalyst. Pd_xSb_y phases ($x = 3$, $y = 3$, $x + y < 6$) are observed from its XRD data. This phase may also be getting reduced at this temperature (350–400 °C) and the presence of carbon moiety (i.e. contribution of spill-over hydrogen) may also be a reason for high intensity of the TPR peak. The BiCCA used catalyst is also found to show similar reduction behavior with lower intensity in this temperature region compared to that of SbCCA catalyst.

All the bimetallic catalysts have exhibited somewhat better stability with respect to reaction temperature than that of monometallic catalysts. Fig. 4 depicts the conversion of CCl₂F₂ and selectivity towards CH₂F₂ and CH₄, respectively as a function of reaction temperature on mono and bimetallic 4 wt.% Pd/CCA catalyst. At a reaction temperature beyond 240 °C, loss of activity can be observed in monometallic catalyst (Pd/CCA). Even up to a reaction temperature of 280 °C, the activity of the monometallic catalyst is higher compared to that of the bimetallic catalysts except on SnCCA, indicating that the second metal has significant influence on the hydrogenolysis activity of the Pd/CCA catalyst.

LaCCA and BaCCA catalysts exhibited similar activity behavior, showing little change in activity with increase in reaction temperature. At 320 °C, the BaCCA catalyst gave better conversion (~30%) than that of LaCCA catalyst (<10%). The poor hydrogenolysis activity associated with these catalysts may be due to the lack of sufficient reducible Pd species on the catalysts. In LaCCA catalyst, most of the Pd is present as an inter-metallic compound, as evidenced from XRD data. La and Ba are mainly structural promoters and may stabilize the support perhaps in our case the support is mostly stabilized with carbon hence we didn't observed any promotional effect in hydrogenolysis. In the present study the catalysts were prepared by co-impregnation method and most of the Pd may have been covered by Ba or

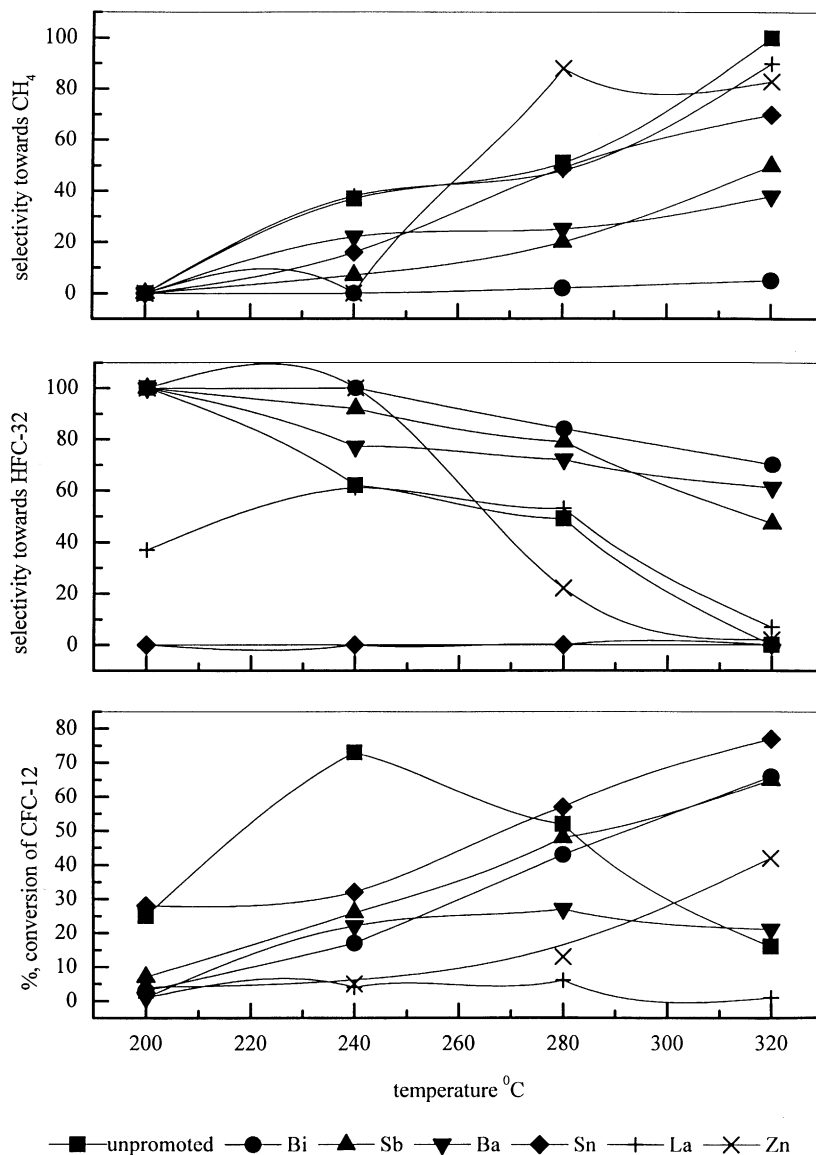


Fig. 4. Hydrodechlorination activity of CCl_2F_2 on bimetallic Pd/CCA catalysts at various reaction temperatures $\text{H}_2/\text{CCl}_2\text{F}_2 = 8$; $\text{GHSV} = 4800 \text{ h}^{-1}$.

La [19,20]. Moreover the Pd–La inter-metallic compound does not appear to be active in the reaction conditions studied. The lack of reducible species in sufficient quantity on this catalyst is revealed by TPR of the catalyst where a high intense peak at $>600^\circ\text{C}$ was observed. Bell and co-workers [19] suggested that during high temperature reduction process La_2O_3

forms LaO_x patches on the surface of the Pd. Hence formation of small LaO_x patches on Pd may reduce the available Pd surface resulting in lower activity for LaCCA in the hydrogenolysis of CCl_2F_2 .

Zn is found to be a good not only in preventing the sintering of Cu metal in methanol synthesis catalyst but also helps in increasing the Cu metal area [21].

However, such type effect is not found with respect to Pd/CCA catalyst. Zn bimetallic catalyst has shown insignificant activity even upto a reaction temperature of 280 °C. The conversion is increased to ~35% at 320 °C. It is very clear from XRD data of used catalyst that large amount of Pd is in the form of PdZn₂. This inter-metallic phase may not be active in the reaction conditions studied. Thus, poor hydrogenolysis activity is observed on ZnCCA catalyst and the increase in the hydrogenolysis activity at a reaction temperature of 320 °C appears to that this inter-metallic phase is some how active beyond 320 °C which can evidenced from the reduction peak at ~350 °C in the TPR of this catalyst.

On Sn bimetallic catalyst, the CCl₂F₂ conversion is increasing linearly with increase in reaction temperature. Pd₃SnC_{0.5} alloy formation can be seen from XRD patterns of reduced and used SnCCA catalyst. TPR profile of used catalyst also indicates a broad reduction peak centered between 200 and 300 °C. An important observation is that Sn bimetallic catalyst is found to show good stability even at a reaction temperature of 320 °C. PdSn/Al₂O₃ bimetallic catalysts have been studied by Coq et al. [7] on C–Cl hydrogenolysis of chlorobenzene. They suggested that the addition of a second metal might affect the catalyst morphology and structure of active phase in two ways: (i) dilution of Pd surface into ensembles of small size, (ii) modification of density states at the Fermi level on surface Pd atoms. However, addition of 0.11 wt.% of Sn to Pd/Al₂O₃ increased the activation energy to 125 kJ/mol in hydrodechlorination of chlorobenzene [7]. Depending on the Pd to Sn ratio, definite inter-metallic compounds like Pd_xSn_y ($x = 1-3$, $y = 1-3$) are reported to be formed [7]. Finally, the authors opined that addition of Sn to Pd decreased the C–Cl hydrogenolysis activity due to decrease in the reducibility of the surface by hydrogen. The HCl produced in the reaction also modifies the surface composition of the catalyst.

Hydrogenolysis activity increased almost linearly with increase in reaction temperature on BiCCA and SbCCA catalysts. Eventhough considerable amount of Pd is present as inter-metallic compounds (Pd_xSb_y) large amount of H₂ consumption is revealed by TPR in between 200 and 350 °C in used SbCCA catalyst implying that easily reducible species were present in the catalyst which facilitate the reaction. In BiCCA used catalyst the relative intensity of the high tempera-

ture peak (200–350 °C) is some what low, eventhough the catalyst exhibited tremendous activity. From XRD data and TPR patterns of the catalyst, some amount of free Pd is also available and this Pd is also contributing to the hydrogenolysis activity resulting in conversions on this catalyst. Ohnishi et al. [10,11] studied the hydrodechlorination of CFC-113 on Pd–Bi bimetallic oxide catalysts supported on alumina and silica and reported high conversions of 80–100% with high selectivity towards trifluoroethene (HFC-1123, ~90%). These authors opined that addition of a second metal like Bi and Tl is modifying the reducibility of the active phase of the catalyst through interaction with Pd enhancing the selective hydrodechlorination ability of the catalyst. However, in case of two carbon system the olefin formation is purely depends on the support acidity, Rüdiger and co-workers in their recent study observed the olefin formation in series of chlorofluoro ethanes to produce oxygenates under hydrolysis and oxidative conditions. In such case its quite difficult to judge the exact effect of second metal in case of olefin either due to the Co-metal or support acidity [22].

Bi, Sb, and Sn bimetallic Pd/CCA catalysts have exhibited a higher performance and stability at higher reaction temperatures. The selectivity of the catalysts for CH₂F₂ and CH₄ are quite different on Bi, Sb and Sn bimetallic Pd/CCA catalysts. It is interesting to observe that Sn bimetallic catalyst gave high selectivity towards CHClF₂ (80% selectivity at 280 °C) where as Bi and Sb bimetallic catalysts have shown high selectivity towards CH₂F₂. The formation of CHClF₂ is dependent on the presence of surface chloride species in the catalyst. From conductivity profiles of the fresh SnCCA catalysts (Fig. 5) recorded during the TPR experiments, considerable chloride evolution was observed over a wide temperature range of 100–550 °C. The hydrochloric acid produced in the course of reaction may not be completely removed by H₂ from the catalyst surface due to high affinity of Sn towards Cl⁻ [7]. Thus, the formation of CHClF₂ is by reaction of CF₂ species with surface HCl over SnCCA catalyst, which the mechanism is also well reported by van de Sandt et al. [23].

Selective hydrodehalogenation ability of Bi and Sb bimetallic Pd/CCA catalysts is found to be high. SbCCA catalyst shows more drop in selectivity towards CH₂F₂ than that of BiCCA, beyond the reaction temperature of 280 °C. Even up to a reaction

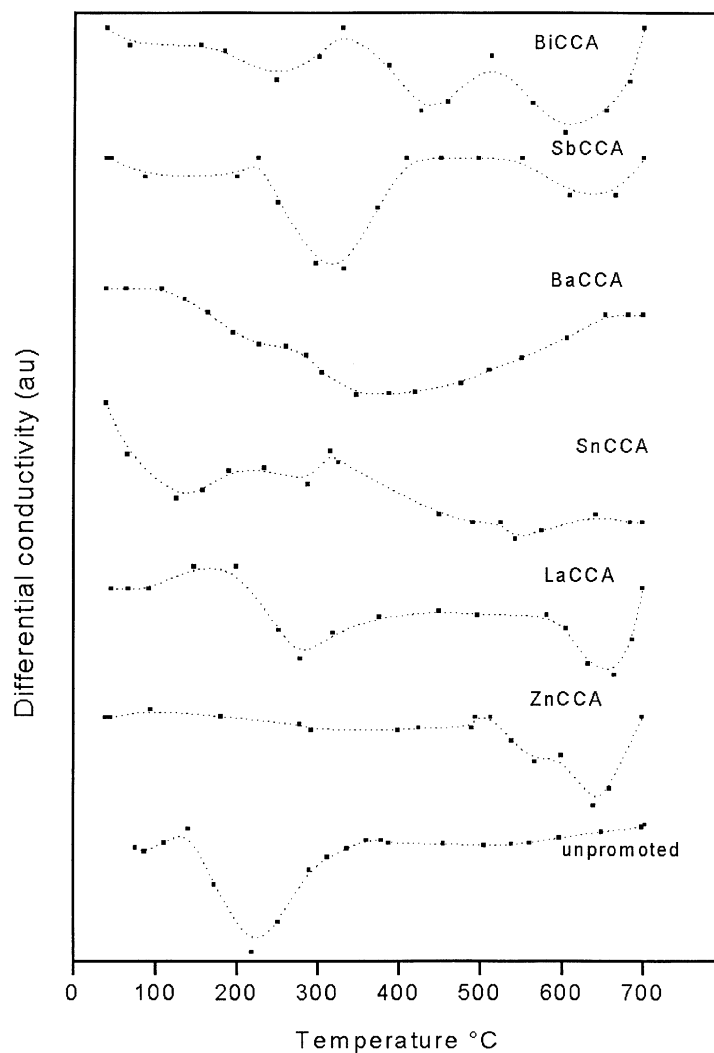


Fig. 5. Conductivity patterns of bimetallic Pd/CCA catalysts.

temperature of 320 °C, the drop in CH_2F_2 selectivity of these catalysts is comparatively less than that of monometallic catalyst. BiCCA bimetallic catalyst not only showed good CCl_2F_2 conversions but also high CH_2F_2 selectivity especially at higher reac-

tion temperatures. CH_2F_2 yields are also high on Bi bimetallic catalyst. Thus, the selective hydrodehalogenation ability and thermal stability can be improved by addition of Bi and Sb metals. Table 2 corresponds to the CH_2F_2 yields of bimetallic Pd/CCA catalysts

Table 2
Difluoromethane yields over CCA supported palladium bimetallic catalysts

Reaction temperature (°C)	Un-promoted	BiCCA	SbCCA	BaCCA	SnCCA	LaCCA
280	25	36	38	19	0	3.2
320	~5	46	30	13	0	0.5

$\text{H}_2/\text{CCl}_2\text{F}_2 = 8$ (molar ratio); GHSV = 4800 h^{-1} .

at 280 and 320 °C reaction temperature. Even at 320 °C BiCCA catalyst gave higher yields (45%) of CH₂F₂.

4. Conclusions

The activity data for the reaction of CCl₂F₂ under hydrogen obtained on the Bi and Sb bimetallic Pd catalysts has shown some novel features and characteristics. In the present study the second metal, in some cases, increased the selective hydrodehalogenation ability of the Pd/CCA catalyst. Bi and Sb bimetallic catalysts exhibited high conversions of CCl₂F₂ with high selectivity for CH₂F₂. Even though, the CCl₂F₂ hydrogenolysis reaction is structure sensitive in nature and favored by larger particle size of Pd, addition of second metal decreased the crystallinity considerable. However, metal–metal interactions appear to play a predominant role in catalyst performance by modifying the selectivity of the Pd catalysts. Addition of a second metal is mainly modifying the reducibility of palladium by the formation of an alloy or an inter-metallic compound. The following factors are mainly responsible for higher yields of CH₂F₂ with high thermal stability of the catalysts.

1. All bimetallic Pd/CCA catalysts show stability even at higher reaction temperatures. Catalyst deactivation is prevented by the addition of a second metal.
2. BiCCA and SbCCA catalysts have shown higher selectivity to CH₂F₂ at all reaction temperatures compared to that of the corresponding unpromoted catalyst.
3. The lower activity of bimetallic catalysts at low reaction temperatures (<280 °C) may be attributed to the fact that some part of Pd is in the form of an inter-metallic compound, which may not be active at the reaction temperature concerned.
4. The presence of a second metal may be preventing the sintering of Pd particle and providing high thermal stability for the catalysts under reaction conditions.

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