

Effect of tungsten addition to Pd/ZrO₂ system in the hydrodechlorination activity of CCl₂F₂

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Abstract

The catalytic activity of Pd on W-ZrO₂ in the hydrodechlorination of CCl₂F₂ was studied by varying WO₃ content. The TPR results of Pd/W-ZrO₂ were related to effects caused by contact with hydrogen. XRD data of spent catalysts shows that there is no change in the structure of zirconia indicating that these catalysts are highly resistant to the corrosive reaction atmosphere. Addition of tungsten to Pd/ZrO₂ system led to the formation of CHClF₂ (HCFC-22) in the hydrodechlorination of CCl₂F₂. Thus, the role of WO₃ is to catalyze the partial dechlorination of CCl₂F₂.

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1. Introduction

Palladium (Pd) supported on oxide supports is known to be active for the hydrodechlorination of chlorofluorocarbons. Most of the literature on the hydrodechlorination of CFCs is cited on alumina supported Pd catalysts [1–6]. It is known that during the hydrodechlorination of CFCs, the oxidic supports undergo transformation into oxy/hydroxy halides because of the liberation of HCl and/or HF during the course of hydrodehalogenation reaction [3]. Thus during the course of hydrodehalogenation reaction both active component and the support get transformed into altogether new structures, thereby modifying the active component–support interaction, acid site distribution, pore structure, etc.

Literature reports reveal that conversion into oxy/hydroxy fluoride is higher in case of Al₂O₃ supported Pd than with ZrO₂ supported Pd catalyst under corrosive reaction condition [3]. The performance of the catalyst is governed by its

aging resistance and it is observed that in supported metal catalysts, the catalyst may be affected by coking, poisoning; and in presence of hydrogen most of the noble metal catalysts undergo sintering during the course of reaction [7–11]. Several literature reports reveal that addition of second metal to the catalyst may prevent sintering and thereby prevent deactivation to some extent like those in bi-metallic catalysts. Some of these studies [12,13] indicate that the second metal modifies the electronic properties of Pd and thereby modifies the active metal reducibility by interaction with it, thus altering the selectivity of the catalyst. It is also known that WO₃/ZrO₂ is a super acid catalyst with an acid strength of $H_0 \leq -14.52$ [14,15].

Notable examples of catalytic reactions over WO₃/ZrO₂ system have been reported in the literature. Zhang et al. reported the activity, selectivity and long-term stability of platinum promoted tungsten-modified zirconia catalysts for the hydroisomerization of long-chain linear alkanes using *n*-hexane as a model compound [16]. Tajima et al. studied the decomposition of CFC-113 over a composite catalyst of Pd/(TiO₂ + ZrO₂) and W/(TiO₂ + ZrO₂) [17].

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The present study highlights the effect of WO_3 addition into Pd/ZrO₂ catalysts for the hydrodechlorination of CFC-12 and this is a first report of the use of Pd/W/ZrO₂ catalytic system for the hydrodechlorination of CCl_2F_2 .

2. Experimental

Tungsten promoted palladium on zirconia catalysts of different compositions were prepared by step-wise wet impregnation method (Table 1). In this method, zirconia support (M/S Loba Chemie, India, SA = 40 m²/g) was impregnated with requisite amounts of aqueous ammonium heptatungstate (M/S Fluka). The excess solution was evaporated on water bath and the samples were dried at 120 °C in air for 12 h followed by calcination in air for 5 h at 450 °C. The calcined mass was then impregnated with Pd using acidified aqueous solution of palladium chloride (M/S Lancaster). These samples were then dried at 80 °C for 24 h and designated as SPWZ fresh catalysts, containing a fixed amount of palladium (4 wt.%) and variable amounts of W. These catalysts were subjected to reduction under H₂ flow (30 ml/min) at 400 °C for 4 h followed by cooling in dry nitrogen flow. The samples thus obtained were used for the surface area and XRD analysis.

XRD patterns of reduced catalysts were recorded on a Siemens D5000 X-ray diffractometer using Ni filtered Cu K α radiation. Surface area measurements have been performed on an all glass high vacuum unit (capable of yielding 10⁻⁶ Torr vacuum) by N₂ adsorption at liquid nitrogen temperature using BET method. Kratos Axis 165 XPS Spectrometer, with Mg K α radiation (1253.6 eV), has been used for obtaining ESCA data. In the ESCA study, C 1s – binding energy value of 285 eV as a reference and the relative atomic sensitivity factors of 5.707, 3.979 and 2.796 for Pd 3d_{5/2}, W 4f and Zr 3d, respectively, for determining surface composition of Pd, W and Zr respectively, have been used. Prior to the ESCA studies, all the catalysts have been reduced in 6% H₂ balance He flow at 250 °C for 4 h. Reaction of CCl_2F_2 in hydrogen over catalysts is carried out in a fixed bed micro-reactor connected on-line to a FID equipped gas chromatograph. An alkali (KOH) trap is connected to the outlet of the reactor in order to remove HCl and HF which are formed

as by-products, before the product mixture is injected into the GC using a six-way sampling valve. The reactivity of the catalysts was carried out at different reaction temperatures ranging from 200 to 320 °C, a molar ratio of H₂/CFC-12 of 8 and a GHSV (gas hourly space velocity) of 4800 h⁻¹. During our preliminary investigations [18], these reaction conditions have been found to be optimum to obtain good activity and selectivity. The products were analyzed under steady-state conditions by GC using a Porapak-Q (3 m long and 1/8" diameter made of SS) column and the product components were identified by GC–MS. The experimental details of the TPR analysis has been discussed elsewhere [18].

3. Results and discussion

3.1. XRD analysis

The XRD patterns (Fig. 1) show Baddeleyite (*d*-values: 3.16, 2.83, 2.62) phase (monoclinic system) of zirconia in all the reduced catalysts. No signals due to Pd or W are observed in any catalysts, indicating that these components are in highly dispersed state. Even though, CFC reaction conditions are very corrosive, where there is every possibility of liberation of HCl and HF, XRD patterns of used catalysts (Fig. 2) show that there is no change in the structure of zirconia indicating that these catalysts are highly resistant to HF or HCl, which are produced during the course of reaction.

3.2. TPR and XPS analysis

The TPR profiles of tungsten promoted Pd/ZrO₂ fresh catalysts at different W/Pd atomic ratio are shown in Fig. 3, which were recorded at a temperature program ramp of 5 °C/min from 30 to 1100 °C. H₂ (5%) in Ar mixture gas was used both as reducing gas and the carrier gas for TCD equipped gas chromatograph (GC).

TPR data reveal that in all the fresh catalysts an endothermic peak centered at 95 °C attributed to the decomposition of β -PdH_x, which forms at room temperature. But it is interesting to observe that the formation of β -PdH_x is delayed in the case of higher loading of tungsten (W/Pd = 2), which may be due to the interaction between PdCl₂ and WO₃.

Table 1
Composition and BET surface areas of Pd/W-ZrO₂ catalysts

S. no.	Catalyst code	W/Pd atomic ratio	W loading (wt.%)	Pd loading (wt.%)	BET-SA (m ² /g)
1	SPWZ1	0	0	4	23
2	SPWZ2	0.1	0.69	4	15
3	SPWZ3	0.2	1.38	4	13
4	SPWZ4	0.4	2.76	4	15
5	SPWZ5	0.6	4.15	4	17
6	SPWZ6	0.8	5.53	4	18
7	SPWZ7	1.0	6.91	4	22
8	SPWZ8	2.0	13.83	4	27
9	SPWZ9	–	6.91	0	34

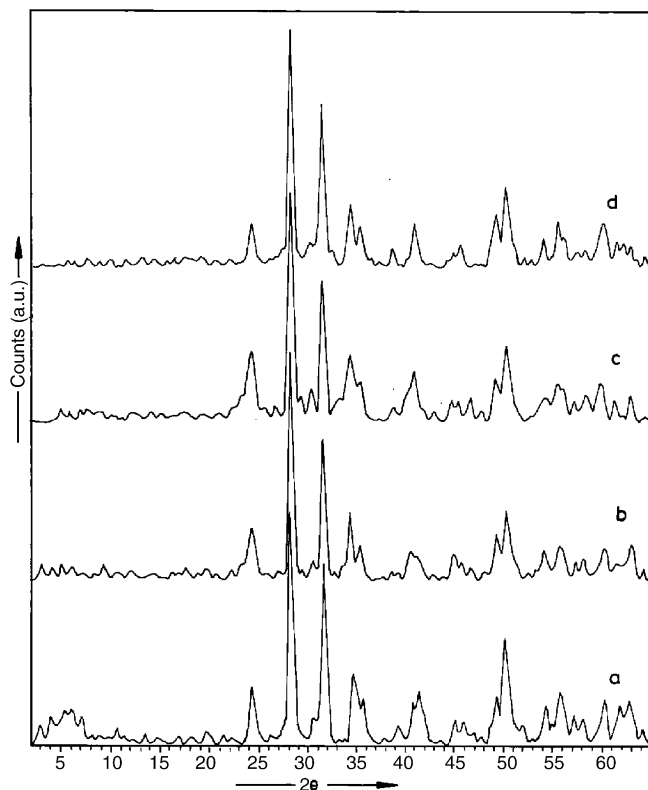


Fig. 1. XRD patterns Pd/W-ZrO₂ reduced catalysts: (a) SPWZ1, (b) SPWZ7, (c) SPWZ8 and (d) SPWZ9.

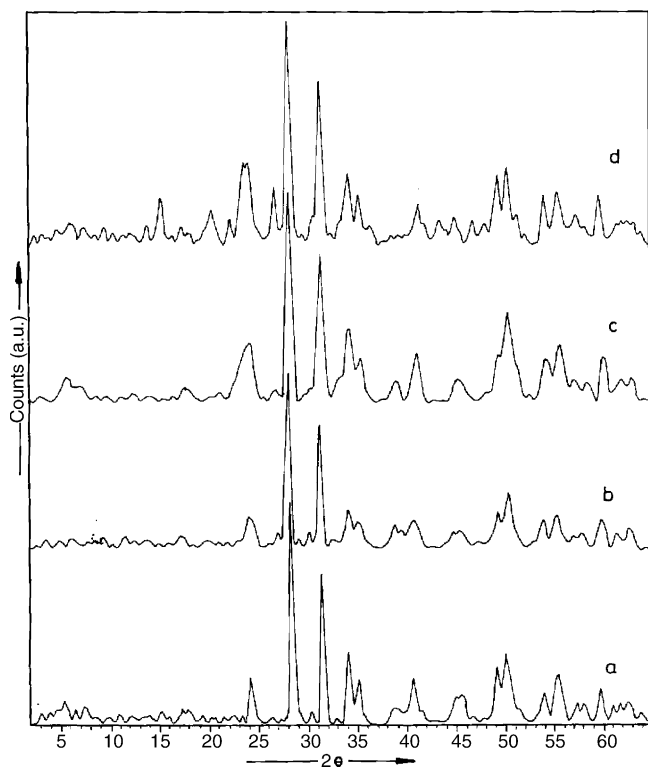


Fig. 2. XRD patterns Pd/W-ZrO₂ spent catalysts: (a) SPWZ1, (b) SPWZ7, (c) SPWZ8 and (d) SPWZ9.

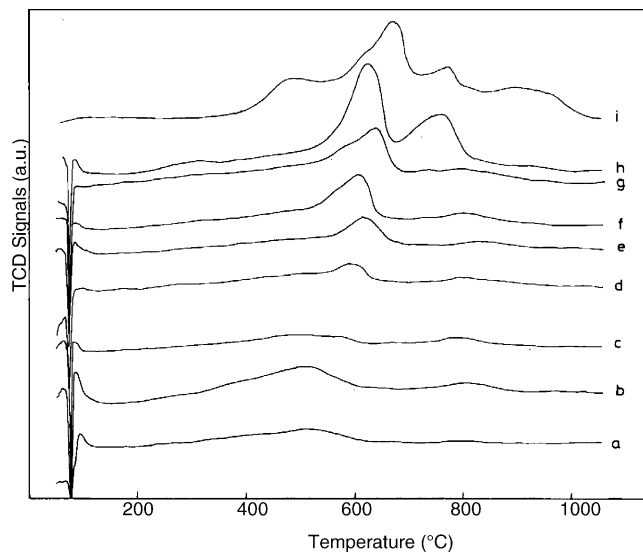


Fig. 3. TPR patterns Pd/W-ZrO₂ fresh catalysts: (a) SPWZ1, (b) SPWZ2, (c) SPWZ3, (d) SPWZ4, (e) SPWZ5, (f) SPWZ6, (g) SPWZ7, (h) SPWZ8 and (i) SPWZ9.

A broad peak centered at a T_{\max} of 525 °C which is shifted to higher temperature region (~630 °C) with increasing W/Pd ratio up to W/Pd = 1 (beyond which the T_{\max} is constant) is observed and attributed to the reduction of ZrO₂.

Another broad peak centered at 785 °C may be attributed to the reduction of WO₃. It is worth noticing that with increasing W/Pd ratio these two high temperature reduction peaks come closer, i.e., shift of ZrO₂ peak to high temperature (525–630 °C) and WO₃ to low temperature (785–765 °C) and the intensity of these peaks also increased with W/Pd ratio. This may be attributed to the interaction between ZrO₂ and WO₃.

Table 2 shows the BE values and the surface composition of Pd, Zr and W, respectively. The Pd 3d_{5/2} BE value is lower in W promoted catalysts compared to that in unpromoted Pd catalyst. Similarly, the BE value of W in WO₃/ZrO₂ is lower than that in Pd-W/ZrO₂. Thus, it is clear that an interaction between Pd and WO₃ might have taken place during the reduction period. Even though SPWZ8 contains more amount of W (13.83 wt.%) than that in SPWZ9 (6.91 wt.%), the surface composition of W (as obtained from XPS data) is lower in SPWZ8 (22 wt.%) than that in SPWZ9 (26%). This indicates that a portion of W in SPWZ8 is in interaction with Pd.

3.3. Activity study

Hydrodechlorination activity of CCl₂F₂ over Pd/ZrO₂, W/ZrO₂ and tungsten promoted Pd/ZrO₂ catalysts is shown in Fig. 4.

In the unpromoted Pd/ZrO₂ catalyst, the conversion of CCl₂F₂ is increased with increase in reaction temperature. Selectivity of CH₂F₂ (HFC-32) also shows a similar trend. However, the predominant formation of CHClF₂ (HCFC-22) is observed on tungsten promoted Pd/ZrO₂ catalysts. At

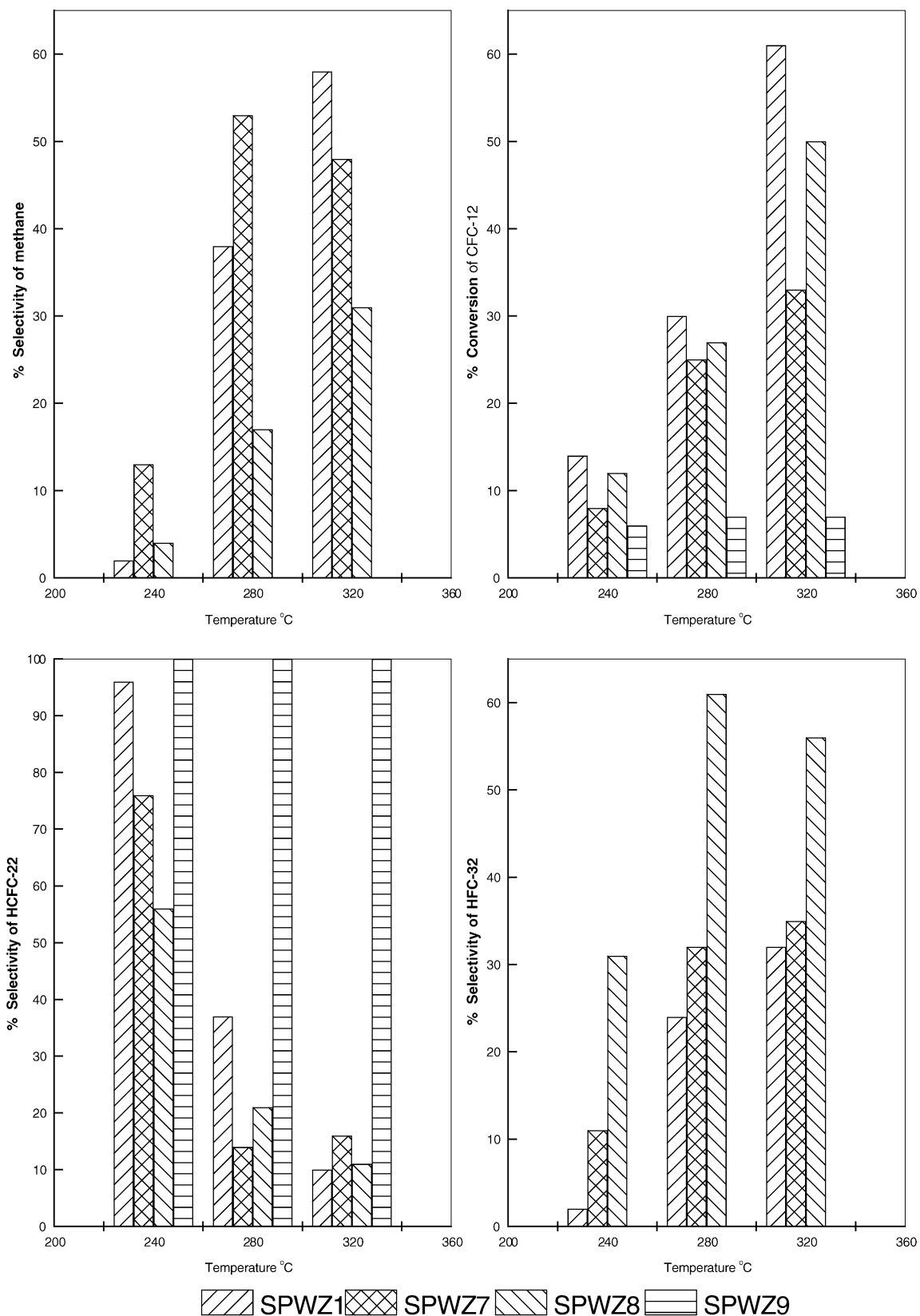
Fig. 4. Hydrodechlorination activity of CFC-12 over Pd-W/ZrO₂ catalysts.

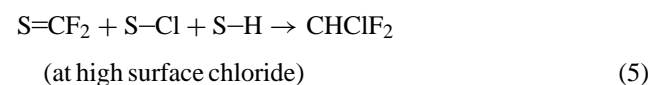
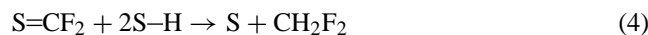
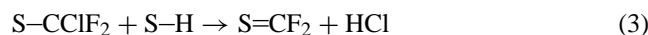
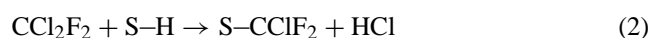
Table 2
Surface composition obtained from XPS data

S. no.	Catalyst code	Binding energy (eV)			Surface composition (mass%)		
		Pd 3d _{5/2}	Zr 3d	W 4f	Pd 3d _{5/2}	Zr 3d	W 4f
1	SPWZ1	333.56	182.75	–	25	47	–
2	SPWZ7	333.12	182.44	35.66	22	41	9
3	SPWZ8	333.30	182.59	Not scanned	19	36	22
4	SPWZ9	–	182.87	36.11	–	44	26

lower loadings of tungsten (from W/Pd = 0.5–0.8) the conversion of CFC-12 is very low (~10%) at all reaction temperatures and the selectivity towards HCFC-22 is 100%. The maximum conversion of 61% and selectivity of 32% to CH₂F₂ is obtained at 320 °C on Pd/ZrO₂. It is interesting to observe that in the W promoted Pd/ZrO₂ catalysts high amount of HCFC-22 is formed. The conversion of the catalyst with W/Pd = 2 is more than that on W/Pd = 1 at all reaction temperatures, though the selectivity to HFC-32 is higher at 280 °C on the catalyst with W/Pd = 2 than at 320 °C. It is known that W/ZrO₂ is a solid acid; it is more acidic than conc. H₂SO₄. The presence of Lewis acidity in the catalyst makes Pd to become more electron deficient which is a key factor in obtaining CH₂F₂ selectivity. In the present case, among the product components, HCFC-22 is very significant. This gives an impression that the acid sites of W/ZrO₂ may be Bronsted in nature. The formation of HCFC-22 may be explained by the associative desorption of *CF₂ species with surface chloride and this behavior of the catalyst is responsible for high selectivity of HCFC-22.

A typical reaction mechanism on the formation of HFC-32 and HCFC-22 through hydrogenolysis of CFC-12 is as follows [19]:

For the formation of CH₂F₂



where S is the catalyst surface.

The type of interaction between W and Pd or between W and ZrO₂ may be different at different loadings of tungsten in Pd/W-ZrO₂ catalysts, which may be governing the behavior of the catalysts towards the selectivity for HCFC-22 and HFC-32.

4. Conclusions

In the hydrodechlorination of CCl₂F₂, the role of W in Pd/W-ZrO₂ catalytic system appears to be to yield

more selectively the partial dechlorinated product, CHClF₂ (HCFC-22).

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