Hydrodechlorination of CFC-12 over novel supported palladium catalysts

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Novel supported palladium catalysts were prepared through organometallic Pd compounds including dichlorobistriphenylphosphine palladium (DCTPPP) and dithiocyanatobistriphenylphosphine palladium (DTTPPP) for the hydrodechlorination of CFC-12. These catalysts exhibited excellent catalytic activities in hydrodechlorination of CFC-12. Particularly, high selectivities of CH_2F_2 formation were achieved over the catalysts, DCTPPP/MgF_2 with 88.1% and DTTPPP/MgF_2 with 85.8%, at a limited conversion level (<5%). No obvious deactivation was observed for DCTPPP/MgF_2 and DTTPPP/MgF_2 catalysts within 60 h. The higher catalytic activity, CH_2F_2 selectivity and catalyst stability may be mainly attributed to high dispersions of palladium.

KEY WORDS: palladium complex; hydrodechlorination; CFC-12; HFC-32

1. Introduction

Selective conversion of chlorofluorocarbons (CFCs), which have been confirmed to be key substances depleting the stratospheric ozone that protects life on the earth against harmful ultraviolet radiation from the sun [1], into valuable products is an attractive route for disposal of CFCs. Thus, hydrodechlorination catalyzed by transition metals, particularly palladium, becomes an elegant solution for transformation of CFCs into hydrofluorocarbons (HFCs), the generally accepted environmentally benign substitutes owing to their similar physical properties to CFCs [2].

Supported palladium catalysts play a crucial role in hydro-dechlorination of CFCs. Al_2O_3, TiO_2, ZrO_2 [3,4], AlF_3 [3,5–8], MgF_2 [9] and carbon [10–12] have been chosen as the supports in the passed few years. In addition, some mechanistic details of the hydrodechlorination of CFCs on intrinsic palladium have been studied by Somorjai and coworkers [13,14]. Even though chemists generally recognize the importance of metallic palladium as the active centers in hydrodechlorination of CFCs, there are, however, some problems such as improvement of the stability of catalysts and selectivities to target products, *i.e.*, HFCs, remaining to be met. Therefore, the development of new catalysts with highly selective dechlorinating activity and high stability becomes the strategy for hydrodechlorination of CFCs.

In this paper, we will report two novel supported palladium catalysts prepared *via* precursors of palladium triphenylphosphine complex $(Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_2(SCN)_2)$ for hydrodechlorination of CFC-12. Our attempt concerns to try to solve the problems mentioned above.

2. Experimental

CFC-12 with high purity (99.9% in purity) was obtained from Zhejiang Juhua Co., Ltd. Hydrogen supplied by gas station of Zhejiang University (99.95% in purity) was purified by molecular sieve before used. $PdCl_2$ was purchased from Shanghai Reagents Company (99% in purity). MgF_2 (AR grade) and triphenylphosphine (AR grade) were commercial products.

Dichlorobistriphenylphosphine palladium ($Pd(PPh_3)_2$–Cl_2, denoted as DCTPPP) was prepared by reacting the desirable amount of $PdCl_2$ with triphenylphosphine in ethanol solution according to [15]. The dithiocyanatobistriphenylphosphine palladium ($Pd(PPh_3)_2(SCN)_2$, denoted as DTTPPP) was prepared *via* DCTPPP mixing with potassium thiocyanate in ethanol solution under stirring and reflux. The structures of DCTPPP and DTTPPP were identified by element analysis and IR spectra.

Heterogenization of the prepared palladium complexes was conducted by means of the incipient wetness technique. Namely, the MgF_2 support was impregnated into a solution of the palladium complex with desirable concentration in chloroform. The obtained catalysts are denoted as DCTPPP/MgF_2 and DTTPPP/MgF_2, respectively. For comparison, a supported palladium catalyst denoted as Pd/MgF_2 was prepared by impregnation of the support MgF_2 into $PdCl_2$ solution. The Pd loading of the catalysts was 2.0% by weight.

Powder X-ray diffraction (XRD) patterns of catalysts after reactions were recorded on D/MAX 2400 X-ray diffractometer using nickel filtered Cu K_α radiation, a scanning rate of 4°/min and tube power of 32 kV × 20 mA were used.

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IR spectra were performed on a Nicolet-470-FTIR spectrometer with a resolution of 4 cm^{-1}. Spectra of support and catalysts were recorded, and then the intensity of the bands associated with the palladium triphenylphosphine complex thereon was obtained by subtracting the spectrum of the support.

X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB MKIII spectrometer with Al K_α X-ray source ($h\nu = 1486.6$ eV) and power 12.5 kV × 20 mA. Before data acquisition, the samples were outgassed for several hours to minimize the surface contamination.

Metal dispersions were determined by hydrogen chemisorption at room temperature using the double isotherm method on an OMNISORP 100CX equipment. The catalyst sample (*ca.* 300 mg) was pretreated in flowing He and H_2 mixture with equal volume ratio at 573 K for 4 h. Then the sample was evacuated at 573 K to less than 10^{-5} Torr for 1 h and cooled to room temperature under the same vacuum. The sample was exposed to H_2 (*ca.* 30 ml/min) at room temperature. The mean particle size of Pd was calculated using the empirical equation developed by Benson *et al.* [16], d (nm) $= 0.9/D$, where D is the dispersion of palladium.

CCl_2F_2 hydrodechlorination reactions were carried out on a fixed-bed microreactor system at atmospheric pressure. The products were analyzed by GC-1002 equipped with a $\varnothing$ 3 mm × 3 m stainless-steel Porapak Q packed column and FID. For a typical reaction, a catalyst loading of *ca.* 100 mg was used. DCTPPP/MgF_2 and DTTPPP/MgF_2 were pretreated in flowing N_2 (60 ml/min) at 470 K for 2 h, and then nitrogen flow was switched to H_2 and CCl_2F_2 with molar ratio $H_2/CCl_2F_2 = 2:1$ at GSVH of 30000 ml(STP)/h g_{cat}. For Pd/MgF_2, a conventional pre-reduction as suggested in literature [9] was carried out in a mixture of nitrogen and hydrogen with ratio of 1 : 1 (v/v) at 573 K for 4 h after being pretreated in N_2 flow (60 ml/min). The other reaction conditions have been controlled as the same in a typical experiment. A relatively higher pre-reduction temperature for Pd/MgF_2 will not essentially affect the metal dispersion according to hydrogen chemisorption. In order to avoid secondary reaction, the conversion of CCl_2F_2 was controlled within 5%. The catalytic activities were normalized as turnover frequencies (TOFs, h^{-1}) based on palladium dispersions. At the same time, the space–time yields (STYs, mmol/g_{Pd} min) of CH_2F_2 were calculated on the basis of Pd loading for comparison.

3. Results and discussion

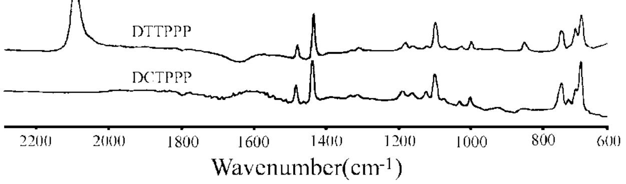
3.1. Characterization of catalysts

The hydrogen chemisorption data, hydrogen uptakes, palladium dispersions and particle sizes of the three catalysts are summarized in table 1. These results reveal a considerable difference in the dispersions of palladium between conventional palladium catalyst Pd/MgF_2 and the two catalysts prepared from organometallic palladium compounds, *i.e.*, DCTPPP/MgF_2 and DTTPPP/MgF_2 indicating a significant effect of the palladium complex precursor on metallic palladium dispersions.

Table 1
A comparison of palladium dispersions and mean particle sizes over supported palladium catalysts.

Catalyst	H_2 uptake (μmol/g_{cat})	Dispersion H/Pd (%)	Mean particle size (Å)
DCTPPP/MgF_2	81.1	86.3	10.4
DTTPPP/MgF_2	89.2	94.9	9.5
Pd/MgF_2	9.3	10.0	90.0

(a) before reaction



(b) after reaction

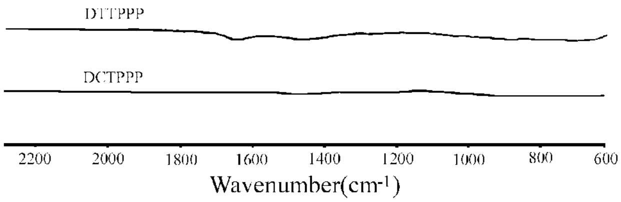


Figure 1. Infrared spectra of MgF_2 supported palladium complexes: (a) after pretreatment in nitrogen and (b) after 10 h reaction for hydrodechlorination of CFC-12.

The FT-IR has been employed to detect the changes in the supported palladium complexes in the hydrodechlorination of CFC-12. Figure 1 (a) and (b) shows the IR spectra of DCTPPP/MgF_2 and DTTPPP/MgF_2 before and after reaction, respectively. The spectra of fresh catalysts (figure 1(a)) revealed that the characteristic absorption band at 2093 cm^{-1} was attributable to SCN vibration, and bands at 1478, 1434, 1098, 749 and 693 cm^{-1} were assigned to the vibration of PPh_3 ligand [15]. However, these bands disappeared on the catalysts after 10 h reaction (figure 1(b)). This suggested forcefully that supported palladium complexes have undergone a dissociation process of ligands during the reaction.

Figure 2 shows the XRD patterns of the used catalysts after hydrodechlorination reaction. For comparison the XRD profile of support MgF_2 has been presented also. The common features of XRD patterns in figure 2 were the appearance of the MgF_2 support phase. In figure 2(d), the corresponding metallic palladium features (Pd(111) and Pd(200)) at 2θ of 39.05° and 45.41° were exhibited for Pd/MgF_2 catalyst. A slight shift of Pd X-ray diffraction to lower 2θ values indicated an expansion of the Pd crystal lattice [17] due to the incorporation of carbon. This was consistent with the previous works [4,10]. However, the correspond-

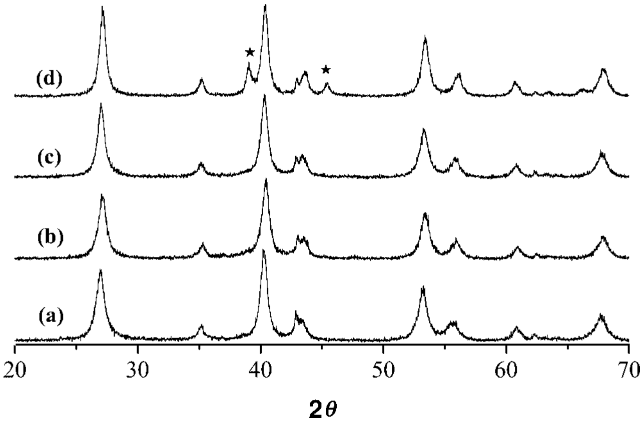


Figure 2. XRD patterns of MgF_2 supported palladium catalysts after 10 h reaction for hydrodechlorination of CFC-12: (a) support MgF_2, (b) DCTPPP/MgF_2, (c) DTTPPP/MgF_2 and (d) conventional Pd/MgF_2 catalyst. (⋆) metallic Pd phase.

ing peaks did not appear in the X-ray diffraction patterns of used DCTPPP/MgF_2 and DTTPPP/MgF_2 (figure 2 (b) and (c)). This indicated the presence of fairly fine particle sizes of palladium in these two catalysts. This was supported by the results from hydrogen chemisorption.

Taken into account the fact that the volume of PPh_3 is much larger than Cl^-, it will make the Pd^{2+} ions deeply apart in contrast to Cl^-. The strong stereo repulsion effect between two complex molecules may result in the occurrence of finely dispersed Pd particles or clusters on the surface of supports. Subsequently, the strong metal–support interactions between Pd and MgF_2 [3–5,7] would stabilize the fine Pd particles or clusters against sintering. The similar result has been reported recently in the case of supported gold catalysts [18–20] prepared by using gold triphenylphosphine complexes as precursors.

3.2. Catalytic performance of supported palladium catalysts

The results of catalytic performance over the supported palladium catalysts prepared by both conventional method and organometallic Pd compounds are summarized in table 2. The time-on-stream behavior of HFC-32 selectivities is shown in figure 3. Figure 4 presents the stability of the catalysts. Besides trace amounts of CH_3F and C_2 hydrocarbons (*e.g.*, ethane), CH_2F_2, CH_4 and $CHClF_2$ were found to be main products, as given in table 2.

For comparison, the catalytic behavior of 2 wt% Pd/MgF_2 prepared by conventional method *via* $PdCl_2$ precursor has been examined also. The results showed that Pd/MgF_2 demonstrated a remarkable deactivation at the initial 10 h reactions, as shown in figure 4. The turnover frequency numbers decreased from 687.7 h^{-1} initially to 381.4 h^{-1} after 10 h on stream (table 2). It should be mentioned that the TOFs obtained on Pd/MgF_2 were at the same order of magnitude as for other conventional supported palladium catalysts, such as 307 h^{-1} for Pd/AlF_3 [3] and 275.4 h^{-1} for Pd/MgF_2 [9]. However, the catalytic activities for both DCTPPP/MgF_2 and DTTPPP/MgF_2 were fairly stable, as presented in figure 4. No obvious deactivation within 60 h on stream was observed in the present reaction conditions.

Table 2
Hydrodechlorination of CCl_2F_2 on supported palladium complex: reaction activity (TOFs), product distribution and space–time yield (STY) of CH_2F_2.[a]

Catalyst[b]	Selectivity (%)			STY of CH_2F_2	TOF (h^{-1})	
	CH_4	CH_2F_2	$CHClF_2$	(mmol/g_{Pd} min)	0.5 h	10 h
DCTPPP/MgF_2	7.4	88.1	4.5	6.20	5.9	51.8
DTTPPP/MgF_2	7.0	85.8	5.3	10.21	0.2	75.8
Pd/MgF_2	17.4	70.7	11.9	4.22	686.7	381.4

[a] Reaction conditions: 470 K, 1 atm, CFC-12/H_2 = 1 : 2 (v/v), GSVH = 30000 ml (STP)/h g_{cat}.

[b] Palladium loading 2 wt%, DCTPPP represents dichlorobistriphenylphosphine palladium, DTTPPP represents dithiocyanatobistriphenylphosphine palladium.

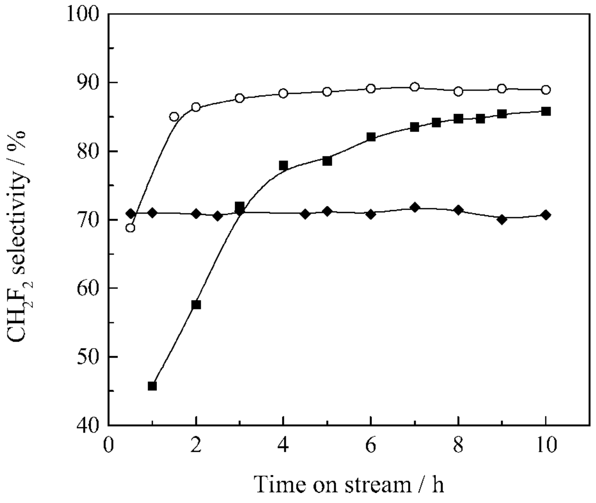


Figure 3. The CH_2F_2 selectivities of supported palladium catalysts as a function of time on stream: (■) DTTPPP/MgF_2, (○) DCTPPP/MgF_2 and (♦) Pd/MgF_2. Reaction conditions were the same as in table 2.

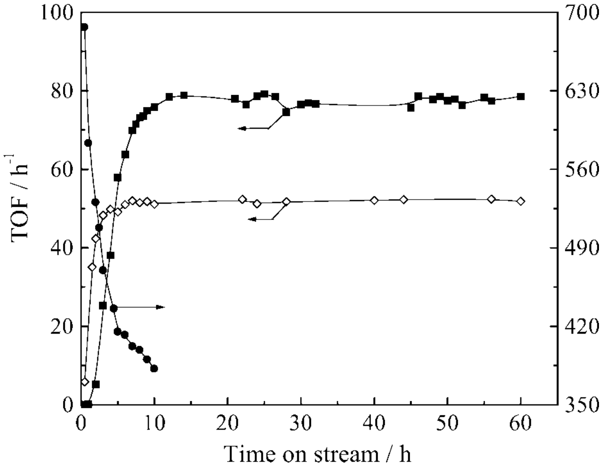


Figure 4. The stability of supported palladium catalyst: (■) DCTPPP/MgF_2, (◇) DTTPPP/MgF_2 and (○) Pd/MgF_2. Reaction conditions were the same as in table 2.

It is apparent from figure 4 that during the initial several hours of reaction the catalytic activities of DCTPPP/MgF_2 and DTTPPP/MgF_2 increased gradually and so did HFC-32 selectivities (see figure 3). These time-on-stream behaviors were mainly attributed to the dissociation of ligands containing sulfur or phosphorus from palladium complexes as exhibited in IR spectra (see figure 1). The element sulfur and/or phosphorus was suspected to be partially removed, however, FT-IR spectra could not present any bands relevant to vibrations of the ligand SCN and PPh_3 for used catalysts. In addition, sulfur was known to affect reaction rates and selectivity for hydrodechlorination [14], and the same was probably true for phosphorus. Thus the remnants S or P might modify the catalytic performance of palladium.

In order to elucidate the possible existence of sulfur and phosphorus on the surface of the catalysts, the XPS spectra of S and P (not shown) were collected over the catalyst sample containing both SCN and PPh_3 ligands in the precursor. The results from X-ray photoelectron spectrometry, however, indicated that the signals near to binding energy 164.05 and 132.9 eV for S_{2p} and P_{2p}, respectively, were too weak to be detected. It indicated sulfur and phosphorus in the ligands were mostly removed *via* the dissociation of the ligands during the present reaction conditions. During this course, the catalytic activity has been enhanced. At the beginning stage, however, the relative low reactivity over the two supported palladium complex catalysts (see figure 4) may be due to the adsorbed sulfur or phosphorus species on the palladium active sites. This phenomenon did not occur on the Pd/MgF_2 sample, because it was prepared free of sulfur or phosphorus.

According to the results by Somorjai and coworkers [14], the effect of S on the catalytic behavior was mainly by blocking palladium active sites by one S atom to one Pd atom. The effect of S and P on the catalytic behaviors in the present conditions would be limited, even though there existed trace amounts of S and P that could not be detected by XPS. Therefore, the partial poisoning or modification by possible remnants S and/or P could be excluded from the main contributors to the unusual selectivity and catalytic stability for DTTPPP/MgF_2 and DCTPPP/MgF_2.

It was suggested that the deactivation of catalysts may be relevant to carbonaceous deposits on the surface of catalyst and strong corrosive acid such as HCl and HF produced during the hydrodechlorination of CFCs [6,21]. As mentioned in [4], the large Pd particles constituted a more capacious sink for carbon than fine particles in highly dispersed catalysts. Larger Pd crystallites contained higher proportion of surface plane sites, which should bind carbon species more strongly than high unsaturated surface sites of lower coordination, like corners and edges [22]. Therefore, fine Pd dispersion seems to be helpful to resist carbonaceous deposit.

On the other hand, the chlorine coverage on the surface of catalyst deeply affected the catalytic activity [13,14,23]. It was reasonably suggested that if the rate-determining step were the cleavage of the first C–Cl bond, the lower reactivity of fine Pd particles than large Pd particles would result in a lower rate of Cl atoms deposition. Nevertheless, the rate of "spillover" of halogen from the metal to the support as suggested in the report [6] would be practically constant. Therefore the concentration of surface chlorine on fine Pd particles would be lower than that on the large one. As a result, the finely dispersed palladium would be more capable to resist corrosive HCl and/or HF.

As given in table 2, Pd/MgF_2 was more active than DCTPPP/MgF_2 and DTTPPP/MgF_2 with a factor of 5–8 in TOF. This is consistent with the results reported by Karpinski and coworkers [4] that a negative dependence of turnover frequencies on Pd dispersions existed in hydrodechlorination of CFC-12. However, the selectivity to HFC-32 over DCTPPP/MgF_2 and DTTPPP/MgF_2 were both dramatically higher ($\sim$88%) than that over Pd/MgF_2 ($\sim$70%) at a low conversion level ($<$5%). It should be mentioned additionally that the space–time yields of HFC-32 on DCTPPP/MgF_2 and DTTPPP/MgF_2 after 10 h on stream were significantly higher than that on Pd/MgF_2.

Coq *et al.* [3,7] suggested that the high selectivity to HFC-32 on supported palladium catalysts such as Pd/Al_2O_3 and Pd/AlF_3 after passivation period might be ascribed to a cooperative effect between metallic Pd and AlF_3 and/or AlF_x species formed inevitably in hydrodechlorination of CFCs. Such an interaction induced electron deficiency between the interface of metallic Pd and the support, and in effect electron-deficient Pd species would bind radicals or reaction intermediates, *e.g.*, CF_2, less strongly, and then produced a high selectivity to HFC-32 [3,7]. According to the hydrogen chemisorption, finely dispersed palladium particles were formed on the surface of MgF_2 support for DCTPPP/MgF_2 and DTTPPP/MgF_2. Therefore there existed strong interactions between metal Pd and the support MgF_2, as suggested in [3,7]. High selectivity to HFC-32 formation would be reasonably interpreted according to the viewpoint of Coq *et al.* [3,7]. The strong metal–support interactions might be also responsible for lower turnover frequency values obtained on DCTPPP/MgF_2 and DTTPPP/MgF_2 rather than on Pd/MgF_2 catalyst. The higher space–time yields of HFC-32 on DCTPPP/MgF_2 and DTTPPP/MgF_2 with higher Pd dispersions could be explained by the fact that the amounts of Pd active sites taking part in the hydrodechlorination on DCTPPP/MgF_2 and DTTPPP/MgF_2 were remarkably greater than that on the Pd/MgF_2 catalyst.

4. Conclusion

Novel supported palladium catalysts prepared *via* palladium triphenylphosphine complexes, including dichlorobistriphenylphosphine palladium (DCTPPP) and dithiocyanatobistriphenylphosphine palladium (DTTPPP) performed high stability and high selectivity to the target product (CH_2F_2) in the hydrodechlorination of dichlorodifluoromethane (CFC-12). FT-IR spectra after reactions clearly show that the supported palladium complexes undergo dissociation of the ligands during the reaction. XRD and H_2 chemisorption exhibited evidence to the formation of finely dispersed metallic palladium over DCTPPP/MgF_2 and DTTPPP/MgF_2 catalysts. It was suggested that the finely dispersed metallic palladium was mainly responsible for the attractive catalytic behaviors of DCTPPP/MgF_2 and DTTPPP/MgF_2.

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