

Supported palladium phthalocyanine catalysts in hydrodechlorination of CCl_2F_2

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Abstract

Supported palladium phthalocyanine was found to be an interesting catalyst with good stability for selective conversion of CCl_2F_2 into CH_2F_2 under flowing hydrogen. Relatively high selectivities towards CH_2F_2 formation over palladium phthalocyanine catalysts with fluoride supports were achieved at limited conversion levels (<10%). Particularly, supported palladium phthalocyanine exhibited excellent stability even at low $\text{H}_2/\text{CCl}_2\text{F}_2$ molar ratio in the corrosive reaction conditions due to the formation of HCl and HF. The fractionally reduced palladium in palladium phthalocyanine was suggested to be the main active site for the catalytic hydrodechlorination. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium phthalocyanine; Hydrodechlorination; CCl_2F_2 ; CH_2F_2

1. Introduction

Extensive attentions have been paid to the elegant hydrodechlorination of chlorofluorocarbons (CFCs) to develop environmentally benign hydrofluorocarbons (HFCs), which were generally suggested to be the alternatives of CFCs [1,2]. Hence, development of effective catalysts for hydrodechlorination of CFCs was the key to obtain high selectivity to desired HFCs. Among these efforts, hydrodechlorination of CCl_2F_2 into CH_2F_2 [3–20] and $\text{CF}_3\text{CCl}_2\text{F}$ into $\text{CF}_3\text{CH}_2\text{F}$ (HFC-134a) [21–33] were extensively investigated, although other CFCs including, $\text{CF}_3\text{CCl}_2\text{F}_2$ [34–36], $\text{CCl}_2\text{FCCl}_2\text{F}_2$ [37–39], CF_3CCl_3 [40] and CClF_3 [41] were also studied in hydrodechlorination reaction. Palladium based catalysts supported on a variety of supports such as alumina [3,4,7,22,37,39],

titania [34], zirconia [34], AlF_3 [3,4,10,34], MgF_2 [11,16], activated carbon [8,21,33,35] were widely used for this reaction, and acceptable selectivity to HFCs and stability were revealed. Particularly, the support effect turned out to be a very important factor for selective removal of chlorine from CFC molecule because the interactions between metal and support favorably modified the electron state of the metal particles [3,4,7,16]. It was claimed that addition of some metal additives greatly improved the catalytic performance of Pd catalysts by geometric and/or electric effects [11,18,19,37–39].

On the other hand, according to the fundamentals of coordination catalysis, introducing the ligands to the catalytic active component (e.g. Pd) was also an alternative manner to modify its electronic state and subsequently its catalytic performance. Although $\text{RhCl}(\text{PPh}_3)_4$ was reported as a catalyst for hydrogenolysis of CF_3CCl_3 in liquid phase [40], however, consideration has been seldom paid to the palladium complex catalysts for hydrodechlorination

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of CFCs in gas phase so far. The idea to utilize thermally, chemically and even photochemically stable palladium phthalocyanine (PdPc) as a catalyst for hydrodechlorination of CFCs in this study was based on the following aspects. First, there was a shortage of supported palladium complex catalysts for hydrodechlorination of CFCs in gas phase. Secondly, the phthalocyanine ring was expected to modify the electronic state of Pd by coordination. Thirdly, metal phthalocyanine derivatives exhibited good stability in demercaptan of petroleum products by Merox process [42,43] and oxidative decomposition of chlorine containing contaminants [44]. It was suggested that Pd phthalocyanine might perform similar behavior in hydrodechlorination of CFCs. Our efforts therefore aimed to attempt to understand the novel behaviors of palladium phthalocyanine as a heterogeneous catalyst in the reaction of hydrodechlorination of CCl_2F_2 . It has not been reported so far.

2. Experimental

Palladium phthalocyanine (PdPc) was prepared by template synthesis from PdCl_2 , phthalic anhydride and urea, and purified by the general procedures for preparation of metal phthalocyanine [45]. Its structure was identified by element analysis, infrared spectrum and ultraviolet–visible spectroscopy. Several materials including AlF_3 (BET surface area $70 \text{ m}^2/\text{g}$), MgF_2 (BET surface area $50 \text{ m}^2/\text{g}$), MgO (BET surface

area $170 \text{ m}^2/\text{g}$), $\gamma\text{-Al}_2\text{O}_3$ (BET surface area $172 \text{ m}^2/\text{g}$) and cocanut activated carbon (BET surface area $1070 \text{ m}^2/\text{g}$) were chosen as support of PdPc. As listed in Table 1, the catalysts were prepared by impregnation of the supports overnight with tetrahydrofuran solution suspending appropriate palladium phthalocyanine under continuous stirring, then dried in vacuum. For comparison, Pd/AlF_3 and Pd/MgF_2 were prepared as reference catalysts by impregnation of support with PdCl_2 solution. All the samples have 1.0 wt.% Pd loading.

IR spectra were performed on a Nicolet-470-FT-IR spectrometer with a resolution of 4 cm^{-1} . Spectra of support and supported PdPc catalysts before and after reaction were recorded, respectively, and then the intensity of the bands associated with palladium phthalocyanine thereon was obtained by subtracting the spectrum of the support.

The ultraviolet–visible absorption spectra were recorded on an Analytikjena Specord 200 ultraviolet–visible spectrophotometer. Before scanning, solid sample of catalysts before and after reaction and support were pressed into pellets, respectively, and the pellet of support was used as a reference.

The reactions of CCl_2F_2 hydrodechlorination were carried out in a fixed bed micro-reactor at atmospheric pressure as described earlier [16]. Namely, the analysis was performed by GC-1002 equipped with $\phi 3 \text{ mm} \times 3 \text{ m}$ stainless steel Porapak Q packed column and FID. The products were identified by GC-MS (HP6890/5973) with HP-1 capillary column. For a

Table 1

Comparison of catalytic performance between supported palladium phthalocyanine and conventional supported palladium catalysts^a

| Catalyst ^b | Conversion (%) | Selectivity (%) ^c | | | Conversion rate ($\text{mmol}(\text{CCl}_2\text{F}_2)/(\text{g Pd}^{-1})\text{min}^{-1}$) | E_a (kJ mol^{-1}) |
|-------------------------------------|----------------|------------------------------|-------------------------|------------------|--|--------------------------------|
| | | CH_4 | CH_2F_2 | CClHF_2 | | |
| PdPc/AlF_3 | 4.86 | 10 | 80 | 10 | 18.26 | 65.6 |
| PdPc/MgF_2 | 2.90 | 10 | 76 | 14 | 10.88 | 73.0 |
| $\text{PdPc}/\text{Al}_2\text{O}_3$ | 1.41 | 13 | 68 | 19 | 5.28 | 74.5 |
| PdPc/MgO | 0.75 | 21 | 58 | 21 | 2.81 | 78.9 |
| PdPc/C | 1.64 | 33 | 61 | 6 | 6.17 | 74.0 |
| Pd/AlF_3 | 5.20 | 25 | 70 | 5 | 19.53 | 60.2 |
| Pd/MgF_2 | 3.26 | 23 | 69 | 8 | 12.23 | 69.5 |

^a After 10 h of operating.

^b Pd loading 1.0 wt.%.

^c Minor products CH_3F and C_2 hydrocarbons were not included. Reaction conditions: weight of catalysts ca. 200 mg, space velocity $15\,000 \text{ ml}(\text{STP})(\text{g cat}^{-1})\text{h}^{-1}$, $\text{H}_2/\text{CCl}_2\text{F}_2$ (v/v) = 2, reaction temperature 523 K.

typical reaction, the supported palladium phthalocyanine catalyst, i.e. PdPc/AlF₃ was preheated in flowing N₂ (60 ml/min) at 573 K for 2 h to remove the adsorbed water, then the temperature declined to 523 K for the subsequent hydrodechlorination reaction. H₂ and CCl₂F₂ were introduced into the reactor with controlled flow and molar ratio (H₂/CCl₂F₂) of 2:1 at a space velocity of ca. 15 000 ml (STP) (g cat⁻¹) h⁻¹. The loading of catalyst was ca. 200 mg for each run. In the case of Pd/AlF₃ and Pd/MgF₂ catalysts, the pretreatment was carried out at 573 K for 3 h in flowing hydrogen to form metallic Pd particles over the support, and then hydrodechlorination reaction was conducted when the reaction temperature was achieved. However, in order to compare the catalytic behaviors of the supported Pd catalysts with supported PdPc catalysts, the reaction conditions such as space velocity and molar ratio H₂/CCl₂F₂ were carefully controlled as the same as in typical run for supported PdPC catalysts, respectively. In order to ensure the reproducible data, each catalyst was tested 2–3 times. The measurement of activation energy was carried out at the condition of steady state. For comparison, the catalytic activity was expressed as molar conversion rate of CCl₂F₂ (mmol (CCl₂F₂) (g Pd⁻¹) min⁻¹). The selectivity was measured at limited conversion levels, generally less than 10%, in order to avoid secondary reactions.

3. Results and discussion

The catalytic activities, product selectivities and apparent activation energies over supported palladium phthalocyanine catalysts and supported palladium catalysts were summarized in Table 1. The time-on-stream behaviors of catalytic activity and CH₂F₂ selectivity over palladium phthalocyanine catalysts including PdPc/AlF₃ and PdPc/MgF₂ and supported palladium catalyst Pd/AlF₃ and Pd/MgF₂ are shown in Fig. 1(a) and (b), respectively.

The results given in Table 1 indicated that the supported palladium phthalocyanines performed interesting catalytic behaviors in the hydrodechlorination of CCl₂F₂. Besides trace amounts of CH₃F and C₂ hydrocarbons, CH₂F₂, CH₄ and CHClF₂ were found to be the major products. The selectivity towards CH₂F₂, the desired product, was 80% over PdPc/AlF₃ and

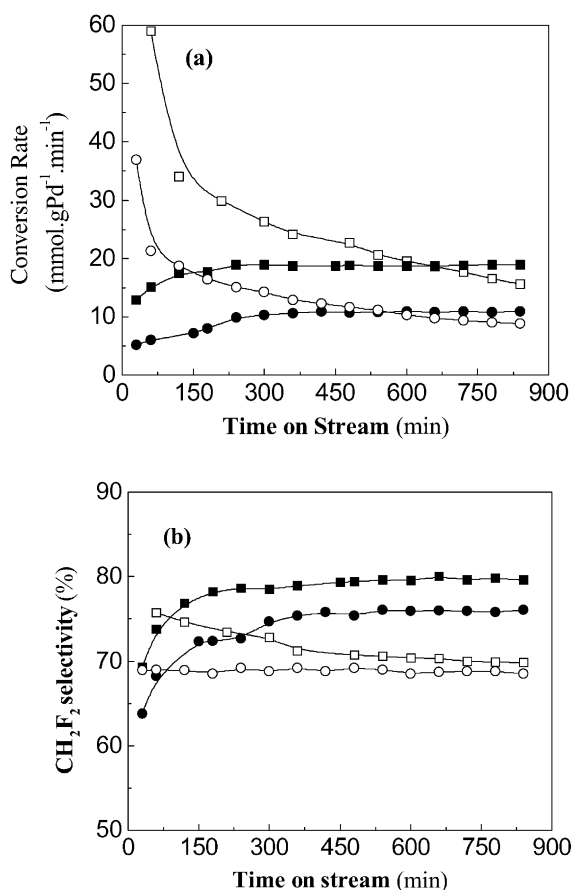


Fig. 1. Comparison of catalytic behaviors between supported palladium phthalocyanine and conventional supported palladium catalyst in hydrodechlorination of CCl₂F₂: (a) overall catalytic activity and (b) selectivity to desired CH₂F₂. PdPc/AlF₃ (■), Pd/AlF₃ (□), PdPc/MgF₂ (●) and Pd/MgF₂ (○); weight of catalysts ca. 200 mg; space velocity 15 000 ml (STP) (g cat⁻¹) h⁻¹; H₂/CCl₂F₂ (v/v) = 2; reaction temperature 523 K.

76% over PdPc/MgF₂, respectively. However, the supported palladium phthalocyanine catalyst with oxides or active carbon as supports exhibited relatively low CH₂F₂ selectivities. It was interesting that the CH₂F₂ selectivities over PdPc/AlF₃ and PdPc/MgF₂ were slightly higher than that over Pd/AlF₃ and Pd/MgF₂. In our experiments, CH₂F₂ selectivities of ca. 70% over Pd/MgF₂ and Pd/AlF₃ were obtained resembling the results from previous reports, e.g. 71% on 2% Pd/MgF₂ [11], 67% on 1.0% Pd/AlF₃ [10,27]. However, CH₂F₂ selectivities of 76–80% over PdPc/AlF₃ and PdPc/MgF₂ are presented in Table 1 and Fig. 1.

The results given in Table 1 also indicated that supported PdPc catalysts have exhibited comparable catalytic activity with conventional palladium catalysts. The conversion rate of CCl_2F_2 over PdPc/ AlF_3 and PdPc/ MgF_2 were close to or higher than that over Pd/ AlF_3 and Pd/ MgF_2 (see Fig. 1(a)). The apparent activation energies on different catalysts were measured as listed in Table 1 for comparison; the results revealed that the less catalytic activity (e.g. over PdPc/ MgO) was followed by the higher apparent activation energy (78.9 kJ/mol). Obviously, the nature of supports essentially affected the catalytic behaviors of supported PdPc. The catalysts with oxide supports, such as MgO and Al_2O_3 , were generally less active than that with fluoride supports. Although activated carbon was common catalyst support, PdPc/C did not present remarked catalytic activity in this study.

In Fig. 1(a), Pd/ AlF_3 and Pd/ MgF_2 demonstrated remarkable deactivation at the initial stage of the hydrodechlorination of CCl_2F_2 ; however, for supported palladium phthalocyanines a period of activation was necessary as shown in Fig. 1(a) also. A steady catalytic activity over supported palladium phthalocyanine catalyst could be achieved within 3–5 h. It was reported that an initial increase in catalytic activity with Pd/ AlF_3 or Pd/ MgF_2 at high $\text{H}_2/\text{CCl}_2\text{F}_2$ molar ratios in hydrodechlorination of CCl_2F_2 was observed [3,11], while contradictory results were also reported by other authors [16,27]. It should be mentioned that the preparation, pretreatment and reaction conditions would essentially affect the catalytic behaviors of catalysts. Particularly, high $\text{H}_2/\text{CCl}_2\text{F}_2$ molar ratio, generally 5–10, was usually chosen in order to avoid the deactivation of conventional supported palladium catalysts [3,11,14]. The present results were obtained at a low $\text{H}_2/\text{CCl}_2\text{F}_2$ molar ratio of 2.

The experimental results suggested that introducing phthalocyanine ring to palladium might be one of the possible factors to improve the stability of catalysts. Thus, the stability of palladium phthalocyanine in hydrodechlorination of CCl_2F_2 became the most concerned matter. In order to obtain more information about stability further, the FT-IR spectra of PdPc/ AlF_3 and PdPc/ MgF_2 before or after reaction (for 10 h) were recorded as shown in Fig. 2(a)–(d). The bands at 1169, 1333, 1421 and 1353 cm^{-1} were assigned to C–C vibration in pyrrole-like structure and 1074 cm^{-1} was one of the most characteristic bands of phthalocyanine skeleton.

The IR spectra of PdPc/ AlF_3 and PdPc/ MgF_2 before and after reaction showed almost no changes at the main bands of Pd phthalocyanine. Particularly, by checking the bands at ~ 1010 and 1540 cm^{-1} which were assigned to the characteristic ring vibration and N–H in-plane bending mode of metal free phthalocyanine, respectively [46,47], the metal free phthalocyanine was not formed on the surface of the catalysts. In other words, the coordination of palladium with the ring of phthalocyanine was fairly stable to resist the severe reaction conditions, although it had been suspected that the formed HCl and/or HF might interact with palladium phthalocyanine and released metal free phthalocyanine.

The ultraviolet–visible spectra as shown in Fig. 3 would give much help to throw light on the nature of the active species. Q bands of absorption spectra due to $a_{1u} \rightarrow e_g$ transitions were found in the range 550–700 nm [48]. The 600 nm band observed for PdPc was due to the configurational interaction between the PdPc molecules that led to the formation of dimeric species. The intensity of this band depended upon the concentration of the dimer formed [49]. The B bands (soret) around 320 nm were assigned to $a_{2u} \rightarrow e_g$ transition [48]. After reaction, these bands (Fig. 3(b)) were found to have no obvious change with respect to the positions. However, appeared broadening of B band (soret) was observed due to the underlying $N p_\sigma \rightarrow e_g (\pi^*)$ transitions in palladium phthalocyanine after reaction [48]. It manifested that after reaction there is strong mixture of the bridge N p_σ and metal $b_{2g} (d_{xy})$, which should affect the ligand field [48]. On the other hand, Kim et al. [50] suggested the broad absorption bands might be also interpreted to the extended π -conjugate system along with the axial coordination.

The observed activation at the initial stage of reaction over palladium phthalocyanine was most probably related to an enforced interaction between two PdPc molecules. Thus the catalytic behaviors of PdPc did not only depend on the metal–metal interaction but also on π – π and d– π overlaps [51]. The arrangement of the planar molecules in close facial proximity with sufficient intermolecular interaction would occur in the presence of hydrogen [51]. At the same time, fractional reduction state of palladium in the arranged face-to-face stacking of PdPc would be more easily produced than in PdPc monomers. The fractionally

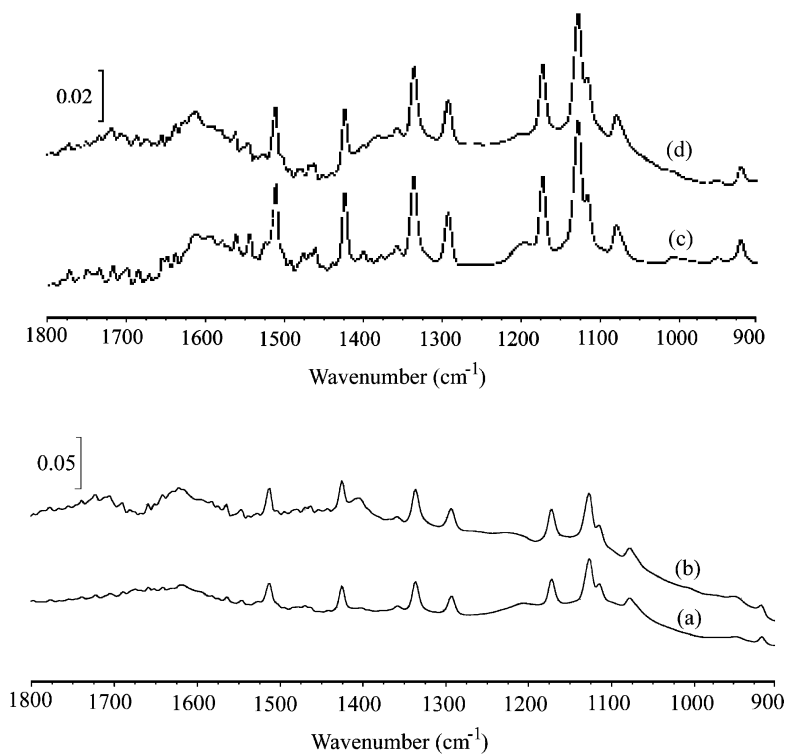


Fig. 2. FT-IR spectra of supported palladium phthalocyanine catalysts (a) PdPc/AlF₃ before reaction, (b) PdPc/AlF₃ after reaction, (c) PdPc/MgF₂ before reaction, and (d) PdPc/MgF₂ after reaction for 10 h. Reaction conditions were the same as in Fig. 1.

reduced palladium seemed to be the main active site in the supported PdPc catalysts.

A probable factor contributing to the deactivation of conventional supported catalysts was carbonaceous

deposit on the surface of catalyst [52]. In this study, it could be suggested that the palladium atoms were separated greatly by phthalocyanine; however, PdPc should be of the similar catalytic activity with

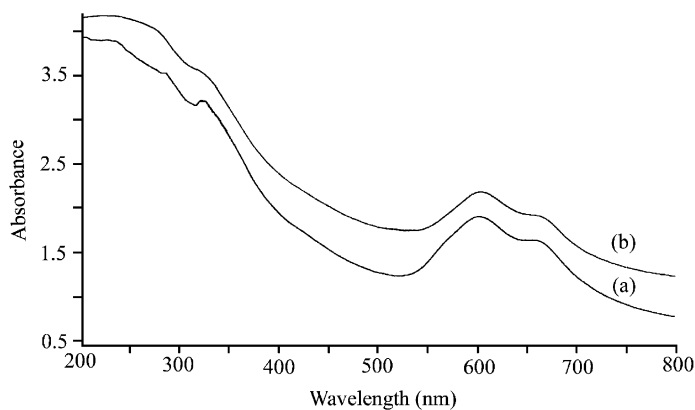


Fig. 3. Ultraviolet-visible spectra of supported palladium phthalocyanine PdPc/AlF₃ before (a) and after (b) reaction of CCl₂F₂ hydrodechlorination for 10 h. Reaction conditions were the same as in Fig. 1.

metallic palladium [53]. As mentioned in literature [7], the large Pd particles constituted a more capacious sink for carbon than fine particles; on the contrary, the finely dispersed Pd in PdPc seemed to be helpful to resist carbonaceous deposit [16].

It is generally accepted that the hydrodechlorination of CCl_2F_2 over supported metallic palladium involved the formation of key intermediate species CF_2 carbene radicals [3,7]. The selectivities for the main products, CH_2F_2 and CH_4 were mainly determined by the ratio between the desorption rate of CF_2 to give CH_2F_2 and the rate formation of other products, e.g. CH_4 [3]. The electronic structure of palladium essentially affects the catalytic performance. The previous works [4] suggested that AlF_3 and AlF_x species can decrease the electron density in palladium sites, and in effect lead to relatively higher selectivity to CH_2F_2 due to the easier desorption of CF_2 from these electro-deficient palladium sites. Similar behaviors over PdPc/ AlF_3 and PdPc/ MgF_2 were performed when considering the different catalytic behaviors on PdPc catalysts with oxides or active carbon supports. Undoubtedly, the coordination of phthalocyanine ring with palladium atoms would decrease the reactivity of palladium, although fractional reduction state of palladium occurred after a period of preactivation. However, due to the high dispersion of Pd in PdPc, the comparable catalytic activity of supported PdPc with supported palladium catalysts might be mainly determined by the larger amounts of Pd active sites taking part in the hydrodechlorination on supported PdPc catalysts. The catalytic mechanism related to this novel supported palladium phthalocyanine catalyst however appears to be unclear yet and deserve further investigations.

4. Conclusion

These preliminary experimental results have revealed that supported palladium phthalocyanine complex exhibited interesting catalytic performance for the reaction of CCl_2F_2 hydrodechlorination in gas phase with acceptable stability and relatively high selectivity to CH_2F_2 as compared with conventional supported palladium catalyst. Palladium phthalocyanine was demonstrated to be fairly stable under the corrosive reaction conditions with the formation of HCl and HF during the reaction. Instead of PdPc

monomers, the fractionally reduced palladium in the face-to-face stacking of PdPc was found to be the main active sites for hydrodechlorination of CCl_2F_2 .

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