Hydrodechlorination of dichlorodifluoromethane over novel CrF₃ supported palladium catalysts

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Novel CrF₃ supported palladium catalysts have been prepared through two different precursors i.e. dichlorobistriphenylphosphine palladium (DCTPPP) and PdCl₂ for the hydrodechlorination of CFC-12. These catalysts exhibited improved catalytic activities in hydrodechlorination of CFC-12 as compared with conventional Pd/γ-Al₂O₃. Particularly, high selectivities (~81%) of CH₂F₂ formation have been achieved over DCTPPP/CrF₃. The improved catalytic performance may be attributed to the nature of support CrF₃ and the formation of fine palladium particles in the catalysts.

Chlorofluorocarbons (CFCs) are the key substances depleting the stratospheric ozone layer that protects life on the earth against harmful ultraviolet radiation from the sun. However hydrofluorocarbons (HFCs) are much less harmful to the environment and have some similar properties with CFCs, and thus it can serve as potential substitutes for CFCs. One of the routes to produce HFCs is hydrodechlorination of their relative CFCs catalyzed by transition metals.

There are a growing number of studies on the catalysis of hydrodechlorination of CFCs ranging from liquid phase to gas phase reaction, the catalysts studied being model catalyst such as Pd foil, single crystal Pd, and Pd black, supported catalysts either noble metal or non-noble metal, group VI transition metal carbides and supported molten salts. Among them, palladium is the most active and the most studied one.

In this note, two novel CrF₃ supported palladium catalysts prepared via different precursors for hydrodechlorination of CFC-12 with improved catalytic activity and CH₂F₂ selectivity by comparing with conventional Pd/γ-Al₂O₃ were reported.

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 use. PdCl₂ was supplied by Shanghai Reagents Company (99% in purity). CrF₃ (AR grade) and triphenylphosphine (AR grade) were commercial products. CrF₃ (BET surface area 35 m²/g) was calcined at 673 K for 5 hr and powdered into 40-60 mesh before use.

Dichlorobistriphenylphosphine palladium (denoted as DCTPPP) was prepared by reaction of desirable amount PdCl₂ with triphenylphosphine in ethanol solution according to literature. The structure of DCTPPP was identified by element analysis and IR spectra.

Heterogenization of the prepared palladium complexes was conducted by means of the incipient wetness technique. Namely, the as prepared CrF₃ support was impregnated into PdCl₂ solution or the solution of palladium complex with desirable concentration in chloroform. The obtained catalysts were denoted as Pd/CrF₃ and DCTPPP/CrF₃ respectively. For comparison, Pd/γ-Al₂O₃ was prepared as reference catalyst by impregnation of support γ-Al₂O₃ (BET surface area 172 m²/g) into PdCl₂ solution as in the case of Pd/CrF₃. The Pd loading of the prepared 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-Kα radiation, a scanning rate of 4°/min and tube power of 32 kV x 20mA were used.

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

CCLI₂F₂ hydrodechlorination reactions were carried out on a fixed bed micro-reactor system at atmospheric pressure as described previously. The products were analyzed in detail by GC-1002 equipped with 0.3mmx3m stainless steel Porapak Q packed column and FID. The products were identified by GC-MS (HP 6890/5973) with HP-1 capillary column. For a typical reaction, a catalyst loading of ca. 100 mg was used. The catalysts were pretreated in...
flowing \( N_2 \) (60 mL/min) at 470 K for 2 hr. After pretreatment, nitrogen flow was switched to \( H_2 \) and \( CCl_2F_2 \) with molar ratio \( H_2/CCl_2F_2 = 2:1 \) at a space velocity of 30000 mL(STP) h\(^{-1}\) gCat\(^{-1}\). The pre-reduction of \( \text{Pd/CrF}_3 \) and \( \text{Pd}/\gamma-\text{Al}_2\text{O}_3 \) was carried out in a mixture of nitrogen and hydrogen with ratio of \( 1:1 \) (v/v) at 573 K for 4 hr, while the other reaction conditions have been controlled as the same in typical experiment. Temperature for activation energy determination was varied in random. In order to ensure that deactivation of catalysts had not occurred during the duration of activation energy determination, the first point in the series was duplicated at the end of the experiment. Temperature for activation energy determination was varied in random. In order to ensure that deactivation of catalysts had not occurred during the duration of activation energy determination, the first point in the series was duplicated at the end of the experiment. The catalytic activities were expressed as the formation rate of \( \text{CH}_2\text{F}_2 \) (mmol gPd\(^{-1}\) min\(^{-1}\)) calculated on the basis of Pd loading for comparison. Selectivities were measured at low conversion levels, usually less than 5% in order to avoid secondary reactions.

**Results and discussion**

**Catalytic performance**

The results of catalytic activity over the \( \text{CrF}_3 \) supported palladium catalysts are listed in Table 1. It can be seen therein that \( \text{CH}_3\text{F}, \text{CH}_4 \) and \( \text{CHCIF}_2 \) were the main products. In addition, \( \text{CH}_2\text{F} \) and \( \text{C}_2 \) hydrocarbons were detected as minor products.

The time on stream behaviour of catalytic activity and \( \text{CH}_2\text{F}_2 \) selectivities are shown in Fig. 1 (a) and (b) respectively. For comparison, the catalytic

![Fig. 1—Comparison of time on stream behaviour of \( \text{CrF}_3 \) supported palladium catalysts with that of \( \text{Pd}/\gamma-\text{Al}_2\text{O}_3 \). (a) space-time yield of \( \text{CH}_3\text{F}_2 \) as a function of time; (b) \( \text{CH}_2\text{F}_2 \) selectivity as a function of time. Reaction conditions: temperature 470 K, \( \text{H}_2/\text{CFC-12(v/v)}=2, \) space velocity 30,000 mL(STP) h\(^{-1}\) gCat\(^{-1}\).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Products(^b)</th>
<th>Formation rate (mmol gPd(^{-1}) min(^{-1}))</th>
<th>Selectivity (%)</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCTPPP/CrF(_3)</td>
<td>( \text{CH}_4 )</td>
<td>0.52</td>
<td>12.3</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{F}_2 )</td>
<td>3.42</td>
<td>80.8</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>( \text{CHCIF}_2 )</td>
<td>0.29</td>
<td>6.9</td>
<td>25</td>
</tr>
<tr>
<td>( \text{Pd}/\text{CrF}_3 )</td>
<td>( \text{CH}_4 )</td>
<td>0.95</td>
<td>18.8</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{F}_2 )</td>
<td>3.61</td>
<td>71.3</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>( \text{CHCIF}_2 )</td>
<td>0.50</td>
<td>9.9</td>
<td>24</td>
</tr>
<tr>
<td>( \text{Pd}/\gamma-\text{Al}_2\text{O}_3 )</td>
<td>( \text{CH}_4 )</td>
<td>1.25</td>
<td>24.5</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{F}_2 )</td>
<td>2.85</td>
<td>55.7</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>( \text{CHCIF}_2 )</td>
<td>1.01</td>
<td>19.8</td>
<td>28</td>
</tr>
</tbody>
</table>

\(^a\)catalytic activity was measured at temperature 470 K, \( \text{H}_2/\text{CFC-12(v/v)}=2, \) space velocity 30,000 mL(STP) h\(^{-1}\) gCat\(^{-1}\).

\(^b\)minor products was not included in.
performance of 2wt.% Pd/γ-Al₂O₃ has been tested as shown in Figs. 1 (a) and (b). The results show that Pd/γ-Al₂O₃ demonstrates deactivation at the initial ten-hour reactions. It should be noted that the time-on-stream behaviour of Pd/γ-Al₂O₃ is similar to the previous results. However, the stability for DCTPPP/CrF₃ is better than that for Pd/γ-Al₂O₃ as shown in Fig. 1 (a). Pd/CrF₃ also demonstrates higher stability than Pd/γ-Al₂O₃ catalyst during the hydrodechlorination of CCl₃F, although its catalytic activity decreases slightly with the time on stream. It should be mentioned additionally that the formation rate of CH₂F₂ over DCTPPP/CrF₃ and PdlCrF₃ are both significantly higher than that over Pd/γ-Al₂O₃ after ten hours on stream, although the initial catalytic activity of the latter is remarkably higher than that of the two formers. At the same time, Fig. 1 (b) exhibits that the selectivities to HFC-32 over DCTPPP/CrF₃ and Pd/CrF₃ are dramatically higher than that over Pd/γ-Al₂O₃ also (∼81% over DCTPPP/CrF₃ and ∼71% over Pd/CrF₃ compared with ∼56% over Pd/γ-Al₂O₃). Thus, the support CrF₃ seems to be a more suitable choice than conventional γ-Al₂O₃. Another characteristic of the catalytic behaviour of DCTPPP/CrF₃ is exhibited that a pre-activation was observed during the first two hour reaction. It manifests that palladium complex DCTPPP was less active than metallic palladium in hydrodechlorination of CFC-12. The improvement of the catalytic activity is mainly attributed to the dissociation of Cl and PPh₃ ligands and then the formation of metallic palladium in the presence of high hydrogen partial pressure. It is supported by the following IR results.

**IR and XRD**

The FT-IR spectra have been employed to detect the changes in DCTPPP/CrF₃ during after the hydrodechlorination of CFC-12. In the IR spectra of DCTPPP/CrF₃ before and after reaction respectively, the 1481 cm⁻¹, 1436 cm⁻¹, 1097 cm⁻¹ bands were assigned to the vibration of PPh₃ ligand in DCTPPP, while these bands disappear on the catalysts after ten hour reaction. This suggests that supported palladium complexes have undergone a dissociation process of ligands during the reaction.

Figure 2 shows the XRD patterns of the used CrF₃ supported palladium catalysts after hydrodechlorination reaction. For comparison the XRD profile of support CrF₃ is also presented [Fig. 2 (a)]. The common features of XRD patterns in Fig. 2 were the appearance of cubic CrF₃ phase. In Fig. 2 (c) the characteristics of metallic palladium (Pd (111) and Pd (200)) at 2θ angles of 38.96° and 45.56° are shown for Pd/CrF₃. A slight shift of Pd X-ray diffraction to lower 20 values indicated an expansion of the Pd crystal lattice due to the incorporation of carbon. Nevertheless, in the X-ray diffraction patterns of used DCTPPP/CrF₃ the corresponding peaks did not appear [Fig. 2 (b)]. This indicated the presence of fairly fine particle sizes of palladium on the surface of DCTPPP/CrF₃ since palladium crystallines were too finely dispersed to give a diffraction signal. Similar results have been reported recently in our previous works.

**Improvement of CH₂F₂ selectivity and stability**

The improvement of CH₂F₂ selectivity and stability is mainly determined by the size of palladium particles and the nature of support CrF₃. The detailed elucidation of the mechanistic route of hydrodechlorination of CFC-12 was not the goal of this study. However, some reasonable discussion based on reaction mechanism would be helpful to recognize the novel catalytic behaviour of CrF₃ supported palladium catalysts further. It's generally accepted that the hydrodechlorination of CCl₃F over supported metallic palladium involved the formation of key intermediate species :CF₂ carbene radicals, and the selectivity for the main products, CH₃F₂ and CH₄ etc., is mainly determined by the ratio between the desorption rate of :CF₂ to give CH₃F₂ and rate formation of other products e.g. CH₄. Coq et al suggested that the high selectivity to HFC-32 on
supported palladium catalysts such as Pd/Al₂O₃ and Pd/AlF₃ after passivation period might be ascribed to a strong interaction between metal Pd and AlF₃ and/or AlF₃ species formed inevitably in hydrodechlorination of CFCs. Such an interaction induces electron deficiency in Pd atoms near to the support, and electron-deficient Pd species will weakly bind radicals e.g. CF₂, and show a high selectivity to HFC-248.

Due to the strong electronegativity of F, strong interactions between metal Pd and CrF₃ might existed. Relatively higher selectivity to CH₂F₂ over CrF₃ supported palladium catalysts i.e. DCTPPP/CrF₃ and Pd/CrF₃ than Pd/γ-Al₂O₃, can be reasonably interpreted according to the viewpoint of Coq et al. Additional, finely dispersed DCTPPP/CrF₃ catalyst, which is characterized by a higher dimension of metal support interface, has higher CH₂F₂ selectivity than even Pd/CrF₃.

As to the stability of catalysts the inhibiting effect of HCl and HF on the hydrodechlorination of CFCs has been established in several investigations. It was shown for hydrodechlorination of chlorobenzene over supported palladium catalysts that a steady state between the chlorination of metallic palladium surface by HCl or chlorobenzene and the reduction of the metallic palladium surface covered by chlorine can be achieved. The reaction order of HCl during CF₃CFCI₂ dechlorination over polycrystalline Pd is reported to be negative. Thus, the stability of catalysts negatively depends on the surface concentration of chlorine.

A higher dimension of metal support interface over DCTPPP/CrF₃ with finely dispersed palladium will produce more electron deficient palladium site. It is less active in hydrodechlorination of CCl₃F₂ than large one, although the total activity of DCTPPP/CrF₃ is comparable with Pd/CrF₃ and even higher than that of Pd/γ-Al₂O₃. If the rate-determining step were the cleavage of the first C-Cl bond as reported in literature, the lower reactivity of fine particles than large particles would result in a lower rate of the deposition of Cl atoms. Nevertheless, the rate of "spillover" of chlorine from the metal to the support as suggested in report would be practically constant for a certain support. So the surface chlorine concentration on fine palladium particle will be lower than that of large one. Then low deactivation rate of catalysts with fine palladium particles will be expected. According to the experimental results, support CrF₃ seems more likely to accept the chlorine spilling from palladium particles. Hence, Pd/CrF₃ is more stable than Pd/γ-Al₂O₃ during the hydrodechlorination of CCl₃F₂.

The deactivation of catalysts may be due to carbonaceous deposits on the surface of catalyst. As mentioned in literature, the large Pd particles constitute a more capacious sink for carbon than small particles in highly dispersed catalysts. Larger Pd crystallites contain 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. Therefore, fine palladium particles seem to be more stable to resist carbonaceous deposit than large ones. However, the experimental result clearly show that Pd/CrF₃ with large palladium particles is remarkably more stable than Pd/γ-Al₂O₃, whether CrF₃ support is also helpful to resist carbonaceous deposition remains a question. Further studies are needed.

In summary, novel CrF₃ supported palladium catalysts prepared via different palladium precursors i.e. dichlorobistriphenylphosphine palladium (DCTPPP) and PdCl₂ had improved stability and higher selectivity to the target product (CH₂F₂) as compared to conventional Pd/γ-Al₂O₃ in hydrodechlorination of difluorochloromethane (CFC-12). FT-IR spectra after reactions clearly show that the supported palladium complexes undergo dissociation of the ligands during the reaction. XRD patterns suggested the formation of finely dispersed palladium over DCTPPP/CrF₃. It was proposed that finely dispersed metallic palladium on the surface of the DCTPPP/CrF₃ catalysts as well as the nature of support CrF₃ were the main contributors to the attractive catalytic behaviours.

References