Hydrodechlorination of dichlorodifluoromethane on carbon-supported Group VIII noble metal catalysts

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Activated carbon-supported Group VIII noble metals formed CF₂Cl₂ oligomerization products under hydrodechlorination conditions. All the catalysts underwent deactivation during first 15-20 h on stream at 250°C independent of the H₂ partial pressure, with steady-state activity following the order: Pt > Pd ≫ Ir > Ru ≈ Os ≈ Rh. The Pd/C catalyst exhibited high selectivity toward C₂–C₃ hydrocarbons (~75% at CF₂Cl₂/H₂ = 1). For the other catalysts except Pt, CF₂ = CF₂ and CH₂ = CF₂ were the main C₂+ products.

Keywords: dichlorodifluoromethane, difluoromethane, ethylene, tetrafluoroethylene, hydrodechlorination, dechlorinative oligomerization, activated carbon, noble metals

1. Introduction

A variety of methods exists to convert chlorofluorocarbons (CFCs) and other partially chlorinated hydrocarbons into environmentally benign materials [1–7]. However, hydrodechlorination to fluorohydrocarbons or hydrocarbons has been studied most extensively [4–7]. Amongst all Group VIII noble metals known for their C–Cl bond cleavage and hydrogenation ability [8], Pd is considered the best catalyst to replace selectively Cl atoms with H atoms in CF₂Cl₂ [9] and chlorohydrocarbons [10]. A much less extensively investigated way to convert the C₁ CFCs into dechlorinated C₂ products such as industrially important monomers C₂H₄ and C₂F₄ was the focus of the present investigation.

Little is known about the catalytic properties required to dimerize halocarbons. Several investigations have shown that both supported Pd [4,9,11] and Pd black [4] catalyze conversion of chlorinated molecules such as CF₂Cl₂ to C₂ hydrocarbons in the presence of hydrogen. Tetrafluoroethylene was formed over Pd–Fe/graphite and Pd–Co/graphite catalysts [12]. In addition, Ru supported on SiO₂ dimerized CF₂–CCl₂ to form corresponding C₄ dimers with 89% selectivity [13]. Alumina-supported Os and Ru were selective toward C₂ chlorocarbons during CCl₄ dechlorination in the presence of hydrogen, whereas Pt and Pd yielded only C₁ products [14]. However, Pt supported on NaY, SiO₂–Al₂O₃, SiO₂, and ZrO₂ was highly selective toward dechlorinative dimerization of CCl₄ (>90% in case of Pt/NaY), but it rapidly deactivated [15]. Chloromethanes oligomerized to molecules containing more than two carbon atoms on supported metals of the first row of Group VIII of the Periodic Table [16,17]. Their dechlorination activity was lower than Group VIII noble metals [18]. Most likely this is due to the higher stability of the corresponding metal chlorides.

In the present research, the hydrodechlorination of CF₂Cl₂ catalyzed by carbon-supported Group VIII noble metals was investigated with particular emphasis on understanding the molecular level catalytic chemistry of dechlorinative CFC dimerization. Because first-row Group VIII metals possess negligible activity below 570 K and increased temperature favors side reactions such as metal-catalyzed support hydrogenation and deactivation due to coking, they were not included in the present study.

2. Experimental

2.1. Catalyst preparation and characterization

Activated carbon (BPL F3, 6 × 16 mesh, Calgon Carbon Corporation) was crushed and sieved. A fraction of 24–60 mesh (1400 m² g⁻¹ surface area, 24 Å average pore diameter, BET data) was used as a support. It was impregnated with an aqueous solution of H₂PtCl₆·6H₂O (Alfa, 38.87% Pt, purity 99.9%, metals basis) or a solution of PdCl₂ (99%), RhCl₃ (98%), OsCl₃·xH₂O (59% Os, all three from Aldrich Chem. Co.), IrCl₃·3H₂O (Alfa, 99.9%, metals basis), RuCl₃·xH₂O (Strem Chemicals, 38.69% Ru, purity 99.9%, metals basis) or 5 N HCl to obtain 0.5% M₈VII/C catalysts. In each case the material was allowed to equilibrate overnight and then was dried at ambient temperature and pressure for 24 h and then at 373 K for 2 h in vacuum (~25 Torr).

BET and chemisorption measurements were conducted with volumetric sorption analyzers ASAP 2010 and ASAP 2010 Chemi (Micromeritics®). The metal–adsorbate ratio was determined from the irreversibly adsorbed CO, H₂ or O₂. The adsorption stoichiometry was assumed to be

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equal to 1 for CO and 2 for both H2 and O2 [19]. For each catalyst CO, H2, and O2 chemisorption as well as titration of adsorbed oxygen with H2 (HT) were performed on the same sample at 308 K and pressures of 100–450 Torr for CO chemisorption and 75–230 Torr for H2, O2 chemisorption and HT. Prior to making these measurements, the catalyst was reduced at 573 K for 2 h and at 623 K for 1 h in H2 flow. This was followed by evacuation for 1.5 h at 623 K. The catalyst was then cooled and CO chemisorption was performed before the catalyst was reduced again at 623 K for 1 h and evacuated for 1.5 h at the same temperature. Then the H2 was chemisorbed and the catalyst was again evacuated at 623 K for 1.5 h. This was followed by O2 chemisorption, evacuation at 308 K for 1 h and H2 titration.

2.2. Catalytic experiments

Hydrodechlorination of CF2Cl2 (PCR, purity >99%) was performed at atmospheric pressure in a stainless-steel flow reaction system consisting of a down-flow quartz microreactor (10 mm i.d.) equipped with a quartz frit to support the catalyst. The reactor zone containing the catalyst was heated by an electric furnace. The catalyst bed temperature was measured and controlled with an accuracy of ±1 K (Omega model CN2011). The gas flows (CF2Cl2, H2 and He) were metered with mass flow controllers (Brooks Instruments model 5850E) and mixed prior to entering the reactor. The reactor effluent was analyzed by on-line GC and by GC/MS to identify the reaction products. The on-line HP GC/MS system consisted of a HP 5890 series II Plus GC equipped with a Fluorol packed column (Supelco) and a flame ionization detector (FID) capable of detecting concentrations >1 ppm for all CFCs, chlorocarbons and hydrocarbons being studied. The on-line HP GC/MS system consisted of a HP 5890 series II Plus GC equipped with a Fluorol column connected to a HP 5972 mass-selective detector.

Prior to reaction, the catalyst was treated with a mixture of H2 (20 ml/min) and He (30 ml/min) (Praxair, each >99.99% of purity) as it was heated from 300 to 673 K at the rate of 5 K/min and held at 673 K for 120 min. The catalyst was then cooled in flowing He to ~353 K and the reactant mixture was introduced. The temperature of the catalyst was then increased to 523 K at the rate of 5 K/min and held constant during the reaction.

The CF2Cl2 was hydrodechlorinated at two CF2Cl2 : H2 ratios, 0.2 and 1. The CF2Cl2 : H2 ratio of 1 is the stoichiometric ratio to obtain dechlorinative dimerization products of CF2Cl2 to form C2F4. The other CF2Cl2 : H2 ratio of 0.2 corresponds to higher partial pressure of H2 than the stoichiometric requirement for total hydrodehalogenation, which is CF2Cl2 : H2 = 0.25. The mass transfer limitations were excluded by verifying that the rate of reaction (μmol of reactant reacted per gram of catalyst per second) for the most active catalyst (Pt/C) remained constant (±10%) for the total flow rates of 5–90 ml/min at constant temperature and concentration. For all experiments the conversion was maintained below 10 mol%.

The kinetics behavior of the catalysts was compared at steady state and at conversion of 0.5–2 mol% of the reactant. The conversion was controlled by adjusting either the total flow rate in the range of 5–90 ml/min or weight of the catalyst from 30 to 150 mg. The selectivities (Si) toward detectable carbon-containing products were calculated as follows:

\[ S_i = \frac{n_i C_i}{\sum_k n_k C_k}, \]

where \( n_i \) and \( C_i \) are the number of carbon atoms in a molecule and the mole fraction of the product \( i \) in effluent gas, respectively. HCl was detected by GC/MS but not quantified. With only the supported Pd catalyst, difluorodimethylsilane was also detected and was attributed to the reaction of the effluent HF with the quartz reactor.

3. Results

3.1. Chemisorption/titration

The results of chemisorption measurements of carbon-supported Group VIII noble metal catalysts, as well as the carbon support are listed in table 1. The dispersion of Pt and Pd on oxide supports is readily obtained both from CO, H2, O2 chemisorption and from hydrogen or oxygen titration [19,20]; whereas H2 chemisorption more accurately estimates dispersions of supported Ru, Rh, Os, and Ir [20–22]. In this investigation the uptake of hydrogen was

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Irreversible gas uptakes and apparent dispersions of M8/C catalysts prepared via metal chlorides.</th>
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<tbody>
<tr>
<td>Catalyst</td>
<td>Uptakes (μmol/g-cat)</td>
</tr>
<tr>
<td>composition (wt%)</td>
<td>CO</td>
</tr>
<tr>
<td>Support</td>
<td>0.0</td>
</tr>
<tr>
<td>0.52Ru</td>
<td>57.0</td>
</tr>
<tr>
<td>0.50Rh</td>
<td>40.5</td>
</tr>
<tr>
<td>0.53Pd</td>
<td>10.9</td>
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<tr>
<td>0.54Os</td>
<td>17.3</td>
</tr>
<tr>
<td>0.52Ir</td>
<td>18.9</td>
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<tr>
<td>0.49Pt</td>
<td>6.8</td>
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negligible on noble metals supported on activated carbon. Krishnakutty and Vannice [23] and Vadlamannati et al. [24] reported similar observations. They showed that for carbon-supported Pd [23] and Pt [24] the equilibrium hydrogen coverage was significantly lower than when these metals were supported on oxides. Carbon monoxide chemisorption is not a good tool for estimating the dispersion of Ru, Rh, Os, and Ir because of uncertainty in CO adsorption stoichiometry due to unknown fraction of the CO adsorbed in a bridged mode [25]. In addition, Ru, Rh, Os, and Ir can form stoichiometric carbonyls with CO/M ratio of 3–5 [26,27] and a fraction of the surface atoms may adsorb more than one CO molecule. The CO/Mₐ ratio for Ru (table 1) confirms this suggestion. All carbon-supported Group VIII noble metals chemisorbed O₂; however, the uptakes were above the allowed stoichiometric limit for all metals except of Pt. Most likely this is because some of the oxygen dissociated on metal surface spills over to the support surface. The results of both oxygen chemisorption and hydrogen titration (table 1) have provided such limited information that a more detailed investigation is required before quantitative dispersion changes are discussed. These dispersion results will be the focus of a forthcoming work.

3.2. Kinetics

The Group VIII noble metals (0.5 wt% Ru, Rh, Pd, Os, Ir, and Pt) supported on activated carbon hydrodechlorinated CF₂Cl₂ and deactivated with time on stream. The initial activity (μmol CF₂Cl₂ g⁻¹ mol⁻¹ s⁻¹ measured at 523 K) increased in the order of Ru < Rh < Pd and Os < Ir < Pt. For all catalysts the conversion with time on stream (TOS) initially increased to a maximum after ~2–8 h. Subsequently, each catalyst deactivated gradually to steady state attained in 15–20 h. (For this particular investigation, a steady state was defined a change in activity per hour was less than 5%). Wiersma et al. observed similar behavior of M₉/C catalysts under conditions of CF₂Cl₂ hydrodechlorination [9]. They suggested that two processes, noble metal redispersion and coking, governed the change in activity. Redispersion induced by molecular chlorine, hydrochloric acid, or other chlorine-containing compounds, such as chlorocarbons or CFCs is well known [28–31]. At the start of reaction the conversion increases because the rate of metal redispersion is higher than the deactivation rate. Then redispersion stops because of equilibration and only coking and possibly halogen accumulation on the catalyst surface determine the conversion changes. The activities at this steady state, calculated on per gram of metal basis are listed in figure 1 for CFC/H₂ ratios of 1 and 0.2. For the second row of Group VIII metals, Pd/C was the most active catalyst (Pd ≫ Ru ≈ Rh) and for the third row, Pt/C was most active (Pt ≫ Ir > Os). The total activity increased for all the catalysts when the CFC : H₂ ratio decreased from 1 to 0.2 (figure 1). The pure support was completely inactive.
The reaction products were classified in two categories: C_1 and C_2+ (oligomerization). The major C_1 products were CH_4, CH_2F_2, CHF_2Cl and CHF_3 (figure 2(A)). Other C_1 products, such as CF_2Cl, CH_2Cl and CH_2F also formed, but in trace amounts (<5% in total). Methane and CH_2F_2 were the main products of CF_2Cl_2 hydrodechlorination on Pt, while CH_2F_2 and CHF_2Cl constituted the main fraction of C_1 products on Pd. Selectivity toward both CH_2F_2 and CH_2 increased toward the right in the series Ru → Rh → Pd and also in Os → Ir → Pt. Monochlorodifluoromethane (CHF_2Cl) was one of the main products of the CF_2Cl_2 + H_2 reaction at CFC/H_2 ratio of 1 on all carbon-supported Group VIII noble metals except Pt. The selectivity toward CHF_2Cl decreased from left to right in both second and third rows of the Periodic Table. The other main C_1 product was CHF_3. The selectivity was approximately the same for Ru, Rh, Os, Ir (40–45 mol%) but was negligible for both Pd and Pt.

Decreasing the CFC/H_2 ratio from 1 to 0.2 increased the selectivity toward CH_4 and decreased the selectivity toward CHF_2Cl for all M VIII/C catalysts (figure 2(B)). The trends in the changes in selectivity were the same as those at the higher CFC/H_2 ratio from left to right in the Periodic Table. The selectivity toward CHF_2Cl decreased from 27 to 4% and that toward CH_4 increased from 3 to 20% in the series Ru → Rh → Pd. The same trend was observed for the other noble metal series Os → Ir → Pt. The selectivity toward CHF_2Cl decreased from 28 to 4% and toward CH_4 increased from 5 to 73% (figure 2(B)). The selectivity toward CH_2F_2 was the highest for Rh and Ir (30% for both). These metals are in the middle of the triads. However, the combined selectivity toward the completely dechlorinated CH_2F_2 and completely dehalogenated CH_4 increased continuously with the higher atomic numbers of the metals in each row of the Periodic Table. The selectivity of Ru/C and Os/C catalysts toward CHF_3 did not depend on the CFC/H_2 ratio. It decreased from 42 to 31% for Rh/C and from 42 to 21% for Ir/C when the CFC/H_2 ratio was decreased from 1 to 0.2.

The theoretical limit on selectivity toward CHF_3 during the halogen exchange reaction of CF_2Cl_2 is double the selectivity toward CH_4, as mandated by the carbon and fluorine balance according to the reaction:

\[
3\text{CF}_2\text{Cl}_2 + 6\text{H}_2 \rightarrow 2\text{CHF}_3 + \text{CH}_4 + 6\text{HCl}
\]

However, the CHF_3 selectivity was 5–20 times higher than the CH_4 selectivity for the Ru, Os, Rh- and Ir-catalyzed reactions (figure 2). This confirms that carbonaceous species formed from CF_2Cl_2 accumulated on the surface of the catalyst during the reaction and may contribute to the rate of deactivation. Another possibility is that F atoms from CF_2Cl_2 react with the support to form CHF_3. However, this is not likely because CHF_3 did not form on Pd/C and Pt/C.

In addition to the reaction pathway for C_1 products, C_1 surface species also oligomerized. The C_2+ compounds produced during CF_2Cl_2 dechlorination catalyzed by M VIII/C are shown in figure 3 for the CF_2Cl_2/H_2 ratio of 1 (A) and 0.2 (B). For the Ru, Rh, Os, Ir, and Pt catalysts the total selectivity toward the oligomerization products was less than 10 mol%. However, the total selectivity for C_2+ products formed on the Pd catalyst exceeded 75 mol% for CFC/H_2 ratio of 1 and 55 mol% for CFC/H_2 ratio of 0.2.

Whereas both saturated and unsaturated C_2–C_3 hydrocarbons constituted oligomerization products of the CF_2Cl_2 + H_2 reaction on Pd/C and Pt/C, the selectivity toward fluorine-containing C_2+ compounds was negligible. A small fraction (<4%) of oligomerization products (probably, C_2–C_3 hydrocarbons) formed on Pd/C was not identified and not included in the overall product distribution presented in figure 3. For the Pd/C, the C_2H_2/C_2H_6 molar ratio decreased in reaction products from 2.0 to 0.4 as the hydrogen partial pressure increased.
For the Ru, Rh, Os, and Ir catalysts only fluorine-containing CF$_2$Cl$_2$ dimerization products CF$_2$=CF$_2$ and CF$_2$=CH$_2$ formed with selectivities of $\leq$5 mol% for each (figure 3). The H$_2$ partial pressure did not significantly affect the selectivity toward dimerization products for metals other than Pd.

4. Discussion

In the early 1920s, Fischer and Tropsch showed that higher molecular weight hydrocarbons could be formed by hydrogenation of CO [32]. In contrast to alternative approaches such as alkylation, the Fischer–Tropsch synthesis centers on the cleavage of a heteroatomic bond and the subsequent hydrogenation and/or oligomerization of the surface CH$_2$ fragments [33–41]. The results of the present investigation suggest that several aspects of the molecular level chemistry associated with geminal halocarbon hydrodehalogenation are analogous to the Fischer–Tropsch synthesis. One of the more significant similarities is that carbene species are also kinetically significant intermediates in the hydrodehalogenation of geminal dihalocarbons catalyzed by Group VIII metals [6,42–44]. The elementary steps that follow the formation of these surface carbene determine their selectivity toward C$_1$ products and the more desirable C$_2$+ products.

The selectivity toward both C$_1$ and C$_2$+ products formed in the dechlorination of CF$_2$Cl$_2$ is strongly influenced by the type of metal catalyst. Based on product distribution (figures 2 and 3) and data available in literature [8,9,45–48], one can conclude that all supported metals used in this study readily dissociate both C–Cl and C–F bonds to provide a surface coverage of C$_1$ species. A necessary subsequent step is the hydrogenation of both F and Cl adatoms which desorb as HCl and HF and regenerate the metal sites. Based on thermodynamics data for Group VIII noble metal chloride reduction with H$_2$ [19] and the general trend of increasing “nobility” of the metal from left to right in the Periodic Table [49,50], it can be concluded that the Cl coverage under hydrodechlorination conditions decreases toward the right in the series Ru $\rightarrow$ Rh $\rightarrow$ Pd and also in Os $\rightarrow$ Ir $\rightarrow$ Pt. The same trend is expected for C coverage. Thus, the activity of Pd and Pt catalyst is most likely attributed to the relatively low Cl and F coverage on their surface, whereas the activity of Ru, Rh, Os, and Ir catalysts is significantly suppressed by strongly adsorbed Cl and F atoms.

The selectivity patterns of CF$_2$Cl$_2$ conversion on supported Group VIII noble metals can be also explained in terms of steady-state halogen coverage. The higher the Cl coverage the lower the driven force of C–Cl bond dissociation. In addition, the probability that a CF$_2$ species will interact with Cl adatoms will be higher. This explains the decreasing selectivity toward CHF$_2$Cl and the increasing selectivity toward CH$_2$F$_2$ from left to right in the series Ru $\rightarrow$ Rh $\rightarrow$ Pd and Os $\rightarrow$ Ir $\rightarrow$ Pt (figures 2 and 3). The higher the F coverage, the higher the probability of interaction of intermediate CF$_2$ species with F adatoms to form adsorbed CF$_3$ species which are subsequently hydrogenated to CHF$_3$ and readily desorb. The high F coverage in case of metals with high F affinity (Rh, Ru, Ir, and Os) is maintained by irreversible degradation of adsorbed CF$_3$Cl$_2$ molecules to surface carbon and halogen atoms, as suggested by the F balance in carbon-containing reaction products presented in figures 2 and 3.

Several factors govern the selectivity towards C$_2$+ products in CO hydrogenation and CF$_2$Cl$_2$ coupling reactions. First, the rate of generation of surface carbene must exceed a certain minimum. If the concentration of these species is low, the probability of coupling to form surface C$_2$ species is low too and mainly CH$_3$ is produced. Second, carbene species must be sufficiently mobile to collide with each other rather than reacting with H adatoms to form C$_1$ products. Third, the partial pressure of H$_2$ must not be too high. At higher H$_2$ partial pressures, the hydrogen surface coverage is higher which increases the rate of CH$_4$ hydrogenation to form CH$_3$. Modifying the electronic structure of metal atoms would influence their ability of catalyzing the surface oligomerization of CH$_2$ species to form higher hydrocarbons. To this end, halogens are highly electronegative elements and adsorption onto the metal surface is expected to modify its electronic structure significantly.

In the CF$_2$Cl$_2$ coupling reaction there is an optimal halogen coverage which provides highest oligomerization activity. Too high a coverage (in case of Ru, Rh, Os, and Ir) results in the blocking of surface sites and low activity. Too low a coverage (in case of Pt) does not provide sufficient electron withdrawal from the metal resulting in a higher hydrogenation rate and thus the formation of C$_1$ products. Relatively low F and Cl coverage on the Pd and Pt surface creates an additional driven force to the dissociation of all C–Cl and C–F bonds in the adsorbed CF$_2$Cl$_2$ molecules. This may be a reason why with Pt and Pd the C$_2$+ reaction products are hydrocarbons formed most likely by surface oligomerization of =CH$_2$ species. On Ru, Rh, Os, and Ir a higher F coverage is expected and surface difluorocarbene (=CF$_2$) species couple either with another =CF$_2$ species to produce CF$_2$=CF$_2$ or with a =CH$_2$ species to produce CF$_2$=CH$_2$; however, the more dominant pathway for the interaction of =CF$_2$ species with F of Cl adatoms to produce CHF$_3$ and CHF$_2$Cl results in low oligomerization selectivity.

In summary, the highest yield of C$_2$+ hydrocarbons and fluorocarbons from CF$_2$Cl$_2$ is produced on metal surfaces that are partially oxidized by surface halogens. Just as in the Fischer–Tropsch reaction with Fe and Co catalysts, the clean metal surface existing at early time on stream is very selective toward CH$_4$ formation [51]. With time on stream the metal surface is equilibrated with the reaction mixture which results in a partially oxidized surface and high oligomerization activity [51–55]. For Fischer–Tropsch, oxygen atoms oxidize the surface. For CF$_2$Cl$_2$ hydrodehalogenation it is halogen atoms. For both reac-
tions surface carbon may also be playing a role. And it is indeed the modified metal surfaces which provide the highest average molecular weight products.

5. Conclusion

The catalytic behavior of activated carbon-supported Group VIII noble metals in the reaction of CF₂Cl₂ hydrodechlorination has been studied as the first step in the effort to understand the chemistry that governs the formation of C₂+ products. All of the catalysts studied deactivated during first 15–20 h on stream at 523 K independent of the CFC/H₂ ratio. The steady-state activity follows the order: Pt > Pd ≫ Ir > Ru ≈ Os ≈ Rh per gram of metal. The Pd/C catalyst exhibited high selectivity toward C₂±C₃ hydrocarbons (~75% at CF₂Cl₂/H₂ = 1). The oligomerization selectivity of other catalysts is under 10% with CF₂=CF₂ and CH₂=CF₂ forming as the main C₂+ products. The high selectivity of the Pd/C catalyst is understood in terms of optimal coverage of the Pd surface with Cl and F atoms that modify the metal particles due to the electron withdrawal effect of halogens.

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