Treatment of residual dichloromethane by gas-phase hydrodechlorination with platinum nanoparticles supported on activated carbon catalysts

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Abstract: - Activated carbon supported catalysts containing platinum nanoparticles as the active phase were prepared to be used in the gas-phase hydrodechlorination of dichloromethane (DCM), which is classified among the most hazardous atmospheric pollutants. Hydrodechlorination (HDC) constitutes an emerging technology for the recycling of chloro-compounds, with the advantages that operates at moderate conditions and leads to much less harmful reaction products. These can be recovered or destroyed by incineration without the inconveniences that the latter shows when it is used to destroy chlorinated compounds (dioxins and phosgene can be formed). The physicochemical properties of the catalysts highly affects their performance, therefore the influence of the surface chemistry of activated carbon, the reduction temperature of the catalysts and the metal load in their final properties and hydrodechlorination activity was investigated. A lower surface acidity of the support leads to a higher stability of the conversion during the operation as it avoids coke formation. The activity per exposed atom (TOF) is increased by increasing the reduction temperature in the range 250-450 °C, as higher Pt⁰/Ptn⁺ proportions were obtained. In the same way, this proportion is higher when increasing metal load up to 2% (w/w) while similar values of platinum nanoparticles sizes were obtained, thus improving, in a significant extent, the dechlorination of the effluent. DCM conversion up to 90% and selectivities to non-chlorinated products higher than 90% were achieved. The catalysts showed a similar activity in a feed DCM concentration range of 1000-3500 ppmv.

Key-Words: atmospheric pollution, dichloromethane, hydrodechlorination, platinum, nanoparticles, carbon, catalysts.

1 Introduction

Chloromethanes (CMs) are volatile organic compounds (VOCs) based on a methane molecule with chlorine atoms. They are widely used on chemical and pharmaceutical industry as solvents and reactants, as well as in aerosols and adhesives, extraction processes, among other. Nevertheless, they are considered important pollutants because of their high stability (remaining in the environment during years) and toxicity [1]. Their emission to the atmosphere contributes to the destruction of the ozone layer, to the formation of photochemical smog and to global warming. Dichloromethane (DCM) is classified among the most hazardous gas pollutants because of its high toxicity and carcinogenic character. Hydrodechlorination (HDC) constitutes an emerging technology for the recycling of chlorocompounds [2]. It operates at moderate conditions leading to much less harmful and valuable reaction products which can be recovered or destroyed by incineration. Precious metals are active catalysts for the carbon-chlorine bond cleavage [3,4]. The use of catalysts based on different precious metals and supports for the HDC of chloromethanes has been reported. In previous studies [1, 5-7], we investigated the HDC of DCM using catalysts based on Pd, Pt, Rh and Ru on activated carbon. Although all the metals named above showed effective in the HDC of the chloromethanes, significant differences were found in both, activity and selectivity. Among them, platinum supported on activated carbon (Pt/C) is very well considered for the hydrodechlorination of dichloromethane because of its high selectivity to non-chlorinated compounds and its superior stability. Catalytic activity, selectivity and stability are related to catalyst structural properties and many variables can affect to these characteristics, such as the
preparation procedure and the support used. The oxidation state of metallic particles on the catalyst surface and the metal particle size play an important role on the catalytic activity of these catalysts in hydrodechlorination [1, 5-9]. The properties of the active phase depend not only on the metal precursor, but also on the type of support. It is accepted that the catalyst support provides a surface on which to disperse the metal allowing higher metal surface areas, which can favor catalytic activity and, probably selectivity and stability. Inorganic and organic materials can be selected as supports. Among them, TiO₂, MgO, Al₂O₃, SiO₂, modified zeolites and activated carbon are the most used in hydrodechlorination [10-13]. However, inorganic materials can be attacked by the HCl formed in the HDC reaction leading to an increase of surface acidity which exacerbates the effects of HCl poisoning and coke deposition. Activated carbons are appropriate supports for this reaction since they are relatively inert to the HCl formed, although the performance of activated carbon is dependent on different variables, such as pore-size distribution and surface oxygen groups. The effect of the support in the hydrodechlorination of organochlorinated compounds has been analyzed from different points of view such as metal-support interactions, the support porous structure or acid-base properties. In a recent review [2], the literature related to supported metal catalysts for hydrodechlorination reactions was investigated. This study shows how metal dispersion, support acid-base properties and electronic interactions with the supported metal can contribute to the catalytic response.

2 Problem Formulation

In previous studies, promising results were found for the gas-phase hydrodechlorination of DCM with Pt/C catalysts. However, the dechlorination degree of the effluent could be increased by the optimization of the catalyst. As stated above, the performance of a catalyst highly depends on their physico-chemical and structural properties and the interaction between the metallic phase and the support. In the current work, with the aim to maximize the detoxification degree of gaseous streams contaminated with DCM using Pt/C catalysts, the influence of Pt loading, catalyst, reduction temperature and the nature of carbon surface in the hydrodechlorination activity, selectivity and stability of the catalysts was investigated. Moreover, in order to extend the contaminant concentration range of the application of the technique, the influence of the feed DCM concentration in the performance of the catalysts was analyzed.

The catalysts behavior was evaluated in terms of dichloromethane conversion (XₘDCM), turnover frequency (TOF) and selectivities to the different reaction products (S). Conversion is defined as the moles of DCM transformed per mol in the feed. Turnover frequency corresponds to the molecules of DCM transformed per atom of metal exposed and time. Selectivity to reaction products is defined as the moles of DCM transformed to give a particular product of the total moles of DCM reacted. The evolution of the catalytic activity upon time on stream was examined in long-term (26 days) experiments.

2.1 Experimental procedures

Carbon-supported platinum catalysts of different platinum loading (in the range 0.5-2.0 % w/w) were prepared by incipient wetness impregnation of three commercial activated carbons (Erkimia S.A. (CE), Merck (CM) and Chemviron (CC)). An aqueous solution containing a pre-calculated amount of metal salt (H₂PtCl₆·6H₂O supplied by Sigma-Aldrich) adjusted to different metal loads, was added drop wise to the activated carbon while stirring, using a carbon particle size of 0.25-0.50 mm. The samples were dried overnight at room temperature and heated up to 100 ºC at a heating rate of 20 ºC·h⁻¹, the final temperature being maintained for 2 h. The catalysts were reduced in situ before use at different temperatures (in the range 250-450 ºC) under H₂ flow (50 cm³·min⁻¹) for 2 h. A heating rate of 10 C·min⁻¹ was used. Hydrogen was supplied by Praxair with a minimum purity of 99.999%.

The porous structure of the catalysts was characterized by N₂ adsorption-desorption at -196 ºC (Tristar II 3020, Micromeritics). The bulk metal content was determined via inductively coupled plasma-mass spectroscopy (ICP-MS) in a Perkin-Elmer model Elan 6000 Sciex system that was equipped with an autosampler (Perkin-Elmer model AS-91). Metal dispersion of the reduced and used catalysts was determined by CO chemisorption at room temperature (PulseChemiSorb 2705, Micromeritics). Transmission electron microscopy (TEM) of the samples was carried out using a JEOL JEM-2100F microscope operating at 200 kV. The surface composition of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) (5700C Multitechnique System, Physical Electronics), using MgKα radiation (hν = 1253.6 eV).

The activity of the catalysts in the hydrodechlorination of dichloromethane was tested in a continuous flow reaction system described...
elsewhere [1], consisting essentially of a 9.5 mm i.d. fixed bed micro-reactor, coupled to a gas chromatograph with a FID detector for the analysis of the reaction products. The experiments were performed at atmospheric pressure using a total flow rate of 100 Ncm⁻³·min⁻¹, a H₂/dichloromethane molar ratio of 100, space-times (τ) of 0.8 and 1.7 kg·h·mol⁻¹ and temperatures of 150-250 ºC. A DCM concentration in the feed of 1000 ppmv was used except when the influence of this parameter was investigated. In that case, the feed concentration was varied in the range 1000-3500 ppmv.

3 Problem Solution

Effect of the activated carbon support

Table 1 summarizes the values of bulk metal content, BET surface area, micropore volume and platinum dispersion (% of surface Pt) of the fresh and used catalyst (26 days on stream in HDC of DCM).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bulk Pt content (%)</th>
<th>S_BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CE Fresh</td>
<td>0.85</td>
<td>1191</td>
<td>0.52</td>
<td>32</td>
</tr>
<tr>
<td>Pt/CM Fresh</td>
<td>0.92</td>
<td>783</td>
<td>0.32</td>
<td>36</td>
</tr>
<tr>
<td>Pt/CC Fresh</td>
<td>1.07</td>
<td>1241</td>
<td>0.53</td>
<td>31</td>
</tr>
<tr>
<td>Pt/CE Used</td>
<td>0.83</td>
<td>1201</td>
<td>0.53</td>
<td>86</td>
</tr>
<tr>
<td>Pt/CM Used</td>
<td>0.91</td>
<td>804</td>
<td>0.32</td>
<td>31</td>
</tr>
<tr>
<td>Pt/CC Used</td>
<td>1.02</td>
<td>1226</td>
<td>0.53</td>
<td>11</td>
</tr>
</tbody>
</table>

All fresh catalysts showed a high BET surface area, although lower in the case of Pt/CM (Merck carbon). No significant differences were observed after used in DCM HDC which discards the blockage of the porous structure by carbonaceous deposits as a cause of the deactivation of the catalyst, as will be explained later in the text.

CO chemisorption results indicate that platinum was fairly well dispersed in all fresh catalysts, with slight differences among them. These differences may be related to the interaction between active phase and support during catalyst preparation, thus to the properties of the active carbon. Erkimia carbon (CE) was examined by N₂-TPD to learn on the surface oxygen groups and the results were compared with those for published Merck (CM) and Chemviron (CC) carbons.[31] The amounts of evolved CO and CO₂ and the CO/CO₂ molar ratio are presented in Table 2. Acidic groups evolve as CO₂ [14]. The overall amount of desorbed CO₂ and the CO/CO₂ molar ratio provides information on the surface acidity of the active carbons. As can be seen in Table 2, the results obtained indicate that the surface of CC has more acidic character than that of CE and CM, in this order. Deconvolution of TPD profiles supports that trend (Table 3). In literature [15-16] it is generally accepted that a higher surface acidity favors higher metal dispersion, since the increase of acidic sites increases the hydrophilic character of the support. However, the differences

<table>
<thead>
<tr>
<th>Active Carbon</th>
<th>Envolving CO groups (µmol/g)</th>
<th>Envolving CO₂ groups (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carboxilic anhydride</td>
<td>Phenol</td>
</tr>
<tr>
<td>CE</td>
<td>-</td>
<td>249</td>
</tr>
<tr>
<td>CM[a]</td>
<td>120</td>
<td>84</td>
</tr>
<tr>
<td>CC[a]</td>
<td>-</td>
<td>28</td>
</tr>
</tbody>
</table>
observed in this case did not lead to significant variations of Pt dispersion. On the other hand, the acid-base properties of the support seem to have a potential effect on the catalyst stability. For example, Early et al. [17] reported that the more acidic the support the more intense deactivation of the catalyst in the hydrodechlorination of CFCs with palladium supported on Al₂O₃, fluorinated Al₂O₃ and AlF₃. The deactivation seems to be caused by the formation of carbonaceous deposits on the surface of the catalyst, which is favored by the acidic character of the support. Similar results were obtained in this contribution that will be explained with more detail later.

The metal dispersion of Pt/CM remained practically constant upon the 26 days of the experiment, whereas substantial changes were observed in the cases of Pt/CE and Pt/CC (Table 1). The latest suffered an important decrease of platinum dispersion consistent with the loss of activity showed by this catalyst, as will be seen below. On the contrary, an important increase of dispersion was observed in Pt/CE which did not show deactivation. This was attributed to re-dispersion of platinum particles during the HDC reaction [6].

Several authors ascribed the re-dispersion of
metallic particles to the effect of HCl which they reported to provoke the formation and volatilization of unstable metallic chlorides followed by metal redeposition.[18, 19] Platinum would be reduced due to the high concentration of H2 introduced as reactant.

TEM images (Figure 1) and the metal particle size distribution (Figure 2) confirm the good Pt dispersion in the fresh catalysts. Average values of 5.8, 1.6 and 2.0 nm were obtained for Pt/CE, Pt/CM and Pt/CC catalysts, respectively. TEM analysis of the used catalysts showed that no significant variations in the particle size and distribution were observed after 26 days on stream in the case of Pt/CM and Pt/CC. These results suggest that the drop of Pt dispersion in Pt/CC after DCM HDC must be due to partial blockage of the active sites with (chloro) carbon species.

The Pt 4f region of the XPS spectra of all the catalysts showed a doublet corresponding to Pt 4f5/2 and Pt 4f7/2. As representative example, Figure 3 depicts the deconvoluted spectrum of the Pt/CE catalyst. The separation between the Pt 4f5/2 and Pt 4f7/2 peaks, due to spin orbital splitting, is a quantized value of 3.33 eV. The Pt 4f7/2 peak lying at around 72.0 eV can be attributed to Pt0 (zero-valent Pt), while the Pt 4f7/2 peak located at around 73.4 eV is related to Ptn+ (electro-deficient Pt) [5]. Table 4 shows the surface Pt composition (as determined by XPS) and the relative proportions of Pt species of the fresh and used Pt/C catalysts. The surface concentration of chlorine and the relative amount of inorganic and organic chlorine obtained from the deconvolution of the Cl2p region are also included. The surface Pt percentages were quite

Table 4. Surface composition of the fresh and used catalyst from deconvoluted XPS profiles.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt0 (% atomic)</th>
<th>Pt0/Ptn+</th>
<th>Cl0 (%)</th>
<th>Cl0/Clin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CE Fresh</td>
<td>0.06</td>
<td>2.8</td>
<td>0.13</td>
<td>4.9</td>
</tr>
<tr>
<td>Pt/CM Fresh</td>
<td>0.07</td>
<td>4.8</td>
<td>0.23</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt/CC Fresh</td>
<td>0.05</td>
<td>3.9</td>
<td>0.33</td>
<td>3.4</td>
</tr>
<tr>
<td>Pt/CE Used</td>
<td>0.04</td>
<td>2.3</td>
<td>0.14</td>
<td>4.4</td>
</tr>
<tr>
<td>Pt/CM Used</td>
<td>0.04</td>
<td>4.1</td>
<td>0.33</td>
<td>2.6</td>
</tr>
<tr>
<td>Pt/CC Used</td>
<td>0.05</td>
<td>2.2</td>
<td>0.32</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Figure 3. Deconvoluted Pt 4f spectra of Pt/CE catalyst after reduction at 250 ºC

Figure 4. Initial conversion of DCM (a) and selectivity to methane and monochloromethane (b) with Pt/CE, Pt/CM and Pt/CC.
similar in all the catalysts, being always Pt0 the prevailing species as a result of the reduction step included in the preparation procedure. The highest Pt0/Ptn+ ratio was found for Pt/CM, followed by Pt/CC and Pt/CE. This ratio diminished somewhat in the used Pt/CE and Pt/CM catalysts and more clearly in the case of Pt/CC, which suffered an important deactivation upon time on stream. Besides, an increase of the relative amount of organic chlorine was found for this catalyst after HDC of DCM. This relationship will be discussed more in detail below.

Figure 4 shows the DCM conversion values achieved with the three catalysts at 1.7 kgcat·h·mol-1 space-time and different reaction temperatures. An important increase in DCM conversion with temperature was observed within the range tested (200-250 ºC). This increase was more pronounced in the cases of Pt/CM and Pt/CC, yielding this second the highest initial conversion (around 87%). In previous works [5,7] it was seen that hydrodechlorination of dichloromethane with the Pt/CE catalyst yielded only methane and monochloromethane, with high selectivities toward methane (>80%) in all cases. Increasing the reaction temperature favors the formation of methane in detriment of monochloromethane. No significant differences in selectivity were found with the two other catalysts using different activated carbon supports (Figure 4).

As stated in a previous work [6], the Pt/CE catalyst showed a high stability upon time on stream. This catalyst did not suffer appreciable loss of activity during 26 days of operation. In the same working conditions (250 ºC and 1.7 kgcat·h·mol-1), long-term experiments were performed with the Pt/CM and Pt/CC catalysts. The results are depicted in Figure 5. Pt/CM resulted active and highly stable in DCM HDC like Pt/CE, being observed a slight increase in DCM conversion after 26 days on stream (a conversion value around 70% was attained).

<table>
<thead>
<tr>
<th>Reduction Temperature (ºC)</th>
<th>Dispersion (%)</th>
<th>Pt0</th>
<th>Pt+</th>
<th>Pt0/Pt+</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>32</td>
<td>73.3</td>
<td>26.7</td>
<td>2.8</td>
</tr>
<tr>
<td>300</td>
<td>25</td>
<td>74.5</td>
<td>25.5</td>
<td>2.9</td>
</tr>
<tr>
<td>350</td>
<td>18</td>
<td>75.9</td>
<td>24.1</td>
<td>3.2</td>
</tr>
<tr>
<td>400</td>
<td>12</td>
<td>83.6</td>
<td>16.4</td>
<td>5.1</td>
</tr>
<tr>
<td>450</td>
<td>6</td>
<td>88.2</td>
<td>11.8</td>
<td>7.5</td>
</tr>
</tbody>
</table>

However, the Pt/CC catalyst suffered an important deactivation upon time on stream, decreasing DCM conversion from 90 to 50%. Selectivity toward methane and monochloromethane (the only reaction products) remained almost constant in all cases. The high stability of Pt/CE was attributed to the small metal particle size after re-dispersion of Pt particles during the reaction and the high Pt0/Ptn+ ratio which allows a greater resistance to poisoning by chloromethane adsorption [6]. As indicated before,
Pt/CM and Pt/CC showed a very small and similar metal particle size prior and after being used in the HDC reaction (Figures 1 and 2). However, Pt/CC exhibited a significant decreased of Pt dispersion (from 31 to 11%) along the reaction, which provokes a loss of activity that cannot be attributed to metal sintering of Pt particles which did not occur (see Figures 1 and 2). When the oxidation state of metal is compared, all the reduced catalysts showed similar Pt\(^{0}/Pt^{n+}\) ratios and even Pt/CC shows a higher proportion of cero-valent Pt than Pt/CE while the latter shows very stable.

Nevertheless, in the case of Pt/CC a great decrease in the proportion of Pt0 was observed after the reaction by means of XPS (Table 4). This is the main active specie in the HDC of chloromethanes with Pt/C catalysts, according to previous works [5,6]. In addition, the Pt/CC catalyst showed a significant increase in the amount of organic chlorine after reaction, whereas no corresponding changes were found for the two other catalysts (Table 4). The increase in the proportion of organic chlorine seems to be related with the poisoning of the active sites with organochlorinated compounds [6, 7, 20] The lower resistance to deactivation of Pt/CC can be ascribed to its higher surface acidity as evidenced by the N\(_2\)-TPD experiments (Table 3). As indicated before, the acidity of the support favors coke deposition and consequently the deactivation of the catalysts as it has been found in other hydrodechlorination reactions. Carbonaceous deposits could be formed rapidly on the more acidic supports and block the active sites, leading to the loss of activity along time on stream [17].

**Effect of reduction temperature of the catalysts**

The effect of the reduction temperature was investigated with the 1% Pt/CE catalyst. The reduction temperature plays an important role in the properties of the catalyst. The most significant effects can be observed in metal dispersion and the relative proportion of Pt species on the surface of the catalyst. Table 5 shows these values.

![Figure 7. TOF, metal dispersion and Pt\(^{0}/Pt^{n+}\) ratio at different reduction temperatures.](image)

![Figure 8. Effect of reduction temperature of Pt/CE on the selectivity and methane formation in HDC of DCM at different reaction temperatures and 1.7 kg·h·mol\(^{-1}\).](image)
It is well known that the reduction temperature is an important parameter which affects the catalyst dispersion on a support. As can be seen in Table 5, the highest Pt dispersion was obtained when the catalyst was reduced at 250 ºC. A higher reduction temperature (above 300 ºC) led to a decrease of the Pt dispersion, due to sintering. On the other hand, the results from XPS show that there is a considerable rise in the relative proportion of zero-valent Pt species with reduction temperature. The HDC of DCM was evaluated at 1.7 kgcat·h·mol⁻¹ space-time. Despite the significant decrease of surface Pt, DCM conversion did not show significant variations with reduction temperature within a fairly wide range (250-400 ºC). Below and above that range a decrease of DCM conversion was observed (Figure 6). Regarding the turnover frequency (TOF) it can be seen a significant increase with the reduction temperature within the range tested (Figure 7). This trend is similar to that of the Pt⁰/Ptn⁺ ratio.

Hydrodechlorination of dichloromethane with the Pt/CE catalyst exclusively yielded methane and monochloromethane, independently of the reduction temperature, with high selectivities toward methane (>70%) in all cases. Methane selectivity increased slightly at the highest reduction temperatures but the lower activity of the catalyst at those reduction temperatures led to a strong decrease of CH₄ formation, as can be seen in Figure 8. Increasing the reaction temperature favors the formation of methane in detriment of monochloromethane.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bulk Pt content (%)</th>
<th>Dispersion (%)</th>
<th>Surface Pt⁰/Ptn⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%Pt/CE</td>
<td>0.43</td>
<td>31</td>
<td>2.7</td>
</tr>
<tr>
<td>1.0%Pt/CE</td>
<td>0.85</td>
<td>32</td>
<td>2.8</td>
</tr>
<tr>
<td>1.5%Pt/CE</td>
<td>1.44</td>
<td>38</td>
<td>2.9</td>
</tr>
<tr>
<td>2.0%Pt/CE</td>
<td>2.11</td>
<td>42</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Table 6. Bulk Pt content, Pt dispersion and relative distribution of Pt species on the surface of the Pt/CE catalysts.

Effect of metal load

The values of bulk metal content, determined via ICP-MS, are in good agreement with the nominal Pt load (Table 6).

No significant differences in platinum dispersion were found with platinum load within the range tested. All catalysts were fairly well disperse with values between 34 and 42%. However, the highest Pt⁰/Ptn⁺ ratio was found in the 2% Pt catalyst whereas no variations were observed below that load (Table 6).

Figure 9 shows the effect of the Pt loading on the catalytic activity at 250 ºC and 0.8 kgcat·h·mol⁻¹ space-time. DCM conversion highly increased with Pt content of the catalyst, mainly at the highest

Figure 9. Effect of Pt content of Pt/CE on DCM conversion and selectivity to methane and monochloromethane at different HDC temperatures.
reaction temperatures, reaching conversion values around 70% at 250 °C with the 2% Pt/CE catalyst. A more pronounced change was observed increasing the Pt load from 1.5 to 2.0%.
The dechlorination of the effluent increased with Pt content. At 250 °C with the 2% Pt/CE catalyst more than 90% methane selectivity was achieved (Figure 8).

Increasing the platinum content of the catalyst, increases the number of available active sites since platinum dispersion was fairly similar in all cases (Table 6).

As shows Table 6, an important increase of the proportion of zero-valent species was observed when increasing Pt load from 1.5 to 2.0%. However, no significant changes can be seen below 1.5%. These results are consistent with the more pronounced increase of DCM conversion within the 1.5-2% Pt range since a higher Pt⁰/Ptn⁺ ratio favors HDC of DCM as indicated before.

Effect of feed concentration

Fig. 9 shows the evolution of DCM conversion, when increasing the DCM feed concentration at a space time of 0.8 kgcat·h·mol⁻¹, using the Pt/CE catalyst. As can be observed, the catalysts remains very effective and even a slight increase of DCM conversion was obtained when increasing its concentration.

A similar product distribution was also observed and therefore a similar dechlorination activity of the effluent.

4 Conclusion

Activated carbon-supported catalysts containing Pt nanoparticles were prepared and have been demonstrated to be effective in the gas phase hydrodechlorination of DCM, at the operating conditions tested (~250 °C, 1 atm). The characteristics of the support play an important role in the activity and stability of the catalysts. Whereas, Pt/CE and Pt/CM maintained their activity upon 26 days on stream, Pt/CC suffered a rapid deactivation. The high stability of the former can be related to a lower superficial acidity of the activated carbon, since the acidity of the support favors coke deposition causing deactivation of the catalysts. Increasing the reduction temperature increases Pt⁰/Ptn⁺ ratio, leading to higher values of TOF for DCM HDC, confirming that Pt⁰ is the main active species. Increasing metal loads to 2% (w/w) leads to an increase of Pt⁰/Ptn⁺ ratio while dispersion remains constant, thus maximizing the dechlorination activity of the catalyst. The effectiveness of the catalyst is maintained in a feed DCM concentration of 1000-3500 ppmv.

References:


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