Valorization of chloromethanes by hydrodechlorination with metallic catalysts

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Abstract

The performance of Pd, Pt, Rh and Ru based catalysts in the hydrodechlorination of chloromethanes to obtain ethane and ethylene was evaluated by means of computational analysis and hydrodechlorination experiments. A computational analysis using density functional theory (DFT) was developed to obtain preliminary insight on the potential catalytic mechanisms for the reactions involved using palladium, platinum, rhodium and ruthenium metallic clusters. Stable catalytic intermediates were obtained by quantum-chemical calculations in the hydrodechlorination of dichloromethane on Pd$_6$ and Rh$_6$ clusters, presenting •CH$_2$ and •CH$_3$ radicals and C$_2$H$_4$, C$_2$H$_6$ and CH$_4$ products. On the contrary, it was not possible to obtain all these stable intermediates using Pt$_6$ and Ru$_6$ clusters. Theoretical analysis revealed lower desorption energies for ethane and ethylene products in Pd$_6$ than in Rh$_6$ clusters, what indicates a favorable selectivity of Pd-based catalyst for desired C$_2$ products. Then, carbon supported catalysts containing these four metals were prepared and experimentally evaluated in the hydrodechlorination of dichloromethane (DCM) and trichloromethane (TCM) at low H$_2$ excess and a reaction temperature range of 150-400 ºC. In agreement with computational results, in experimental tests, the Pd based catalyst showed the best performance for the hydrodechlorination of chloromethanes to obtain C$_2$ products, followed by Rh. Ru and Pt have a poor performance, in special Pt based catalyst, which shows almost no selectivity to C$_2$ products. This computational and experimental study emphasizes, for the first time, the good performance (high activity and selectivity) of Pd carbon supported catalysts in the valorization of chloromethane compounds to obtain C$_2$ hydrocarbon products.

Keywords: valorization, hydrodechlorination, dichloromethane, chloroform, Pd, Rh, Pt, Ru
1. Introduction

Chloromethanes constitute very dangerous waste products from many industrial processes, they are very toxic and carcinogenic, moreover, they contribute to global warming, the depletion of the ozone layer and the formation of photochemical smog [1-4]. Despite their harmful effects, and because of their particular physical and chemical properties, they are still widely used in industry, and large amounts are released in residual effluents through liquid and gas streams. There are several technologies available for the treatment of these compounds [5,6], however their reuse for the production of valuable hydrocarbons would be more interesting.

On the other hand, the petrochemical industry has a great importance in the global economy. World society faces a growing need for a series of organic compounds as starting reagents for chemical industries such as the plastics, pharmaceutical and fine chemical sectors. At present, the transformation, or refining, of petroleum constitutes the major source of these vital starting reagents. However, the exploitation of oil as a feedstock for energy production and petrochemicals shows several problems like environmental pollution or supply problems. This leads to the necessity of exploring alternative raw materials. Proven natural gas reserves are significantly higher than those of oil, it is a less pollutant compound, and moreover, methane (the main component of natural gas), can be obtained from renewable sources. The development of efficient routes for the production of higher hydrocarbons from renewable feedstocks and, in the medium term, from methane transformation is becoming a critical issue and a challenge for the present century. A new approach involves the use of chloromethanes. These molecules are considerably more reactive than methane and could be converted by catalytic dechlorination or hydrodechlorination into valuable products such as light olefins. In recent literature [7-15], a new route based on the dechlorination of monochloromethane (MCM) to olefins is been
investigated (See scheme 1). MCM can be formed from methane and the hydrogen chloride obtained from the dechlorination of MCM.

\[
\text{Scheme 1}
\]

\[
\begin{align*}
\text{CH}_3\text{Cl} & \rightarrow \frac{1}{2} \text{C}_2\text{H}_4 + \text{HCl} \\
\text{CH}_4 + \text{HCl} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}
\end{align*}
\]

This process would overcome the inconvenience of the costly production of syngas [16,17] needed for Fischer-Tropsch and MTO or MTHC processes [18]. However, chloromethanes as dichloromethane (DCM) and chloroform (TCM) are obtained as by-products and their conversion to valuable hydrocarbons is necessary to make the process suitable for practical application [19]. Other inconveniences found in these studies, which use catalytic materials like ZSM-5, HZSM-5, SAPO-34 or HSAP-34 is the rapid deactivation of the catalyst which is a limiting factor for the application of this technology. Deactivation of the catalysts occurs by oligomerization of hydrocarbons and the formation of carbonaceous deposits which cause the blockage of the catalysts pores. The formation of carbonaceous deposits is exacerbated by the acidity of the catalysts, the high reaction temperatures used (up to 500 °C) and the absence of hydrogen.

Currently, the hydrodechlorination studies reported in the literature are focused on reducing the toxicity of industrial effluents and there are very few studies dealing with their use in the production of hydrocarbons [19]. In previous studies [20-23], where we investigated the hydrodechlorination of chloromethanes for the treatment of residual gas streams using supported metal catalysts (Pd, Pt, Rh and Ru), interesting results were found suggesting the possibility of their use for the production of hydrocarbons higher than methane. At the conditions employed in these studies, methane was usually obtained as the main reaction
product, but depending on the catalyst composition, their physicochemical properties and the reactant used, significant proportions of hydrocarbons of up to four carbon atoms were obtained. In other studies [24,25], molecular simulation was used to know about the capacity of metals to adsorb the HDC reactants on the surface, and it was found to be an effective tool to explain the performance of the different metals in the hydrodechlorination of chloromethanes.

The aim of this work is to evaluate the ability of different metals (Pd, Pt, Rh and Ru) for the coupling and hydrodechlorination of two molecules of chloromethanes on metal surfaces in order to develop efficient catalysts for the valorization of chloromethanes wastes to obtain C₂ and C₃ hydrocarbons of industrial interest. For that purpose, a quantum-chemical study, based on Density Functional Theory (DFT) framework, was performed to analyze the presence and stability of catalytic intermediates potentially involved in the catalytic mechanisms for evolving from reactants to products, using DCM as the model reactant and Pd, Pt, Rh and Ru clusters with six metal atoms (M₆). As promising results were obtained with some of the metals, experimental hydrodechlorination studies of DCM and TCM with model catalyst prepared from the cited metals and a commercial carbon as the support were performed. The high surface area of the activated carbon used favor the dispersion of metal particles, and the no-acidic character of its surface hinder the formation of carbonaceous deposits at the high temperatures used in the experiments. The operating conditions were adjusted to favor the formation of C₂ and C₃ hydrocarbons. Higher reaction temperatures (up to 400 ºC) and lower hydrogen/chloromethane molar ratio (10) than those used in previous HDC studies were selected.

2. Experimental

2.1. Computational Methods
All computational studies were performed with the Gaussian 09 [26] series of program. The transition metal clusters present a great number of electrons, which reorganize deeply the atomic electron density, so we have simulated palladium, platinum, rhodium and ruthenium clusters using DFT methods, concretely the B3LYP functional, which combines Becke’s three parameter nonlocal hybrid exchange potential [27] and the nonlocal correlation functional of Lee, Yang and Parr [28]. The chemical inert core orbitals of metal clusters were described with the effective core potentials of Hay and Wadt [29], which include relativistic effects on valence electrons, while the external orbitals were represented with a double-ζ basis set using Dunning/Huzinaga full double-ζ basis set (Lanl2DZ), basis set also used for the rest of atoms of the compounds involved in this work. Thus, all the simulations were conducted at B3LYP/Lanl2DZ computational level, which has been proved to be reliable for system involved Pd atoms [24,25, 30]. Full geometry optimization was done for isolated reactants and products, and catalytic intermediates. In this work, $M_6$ clusters were used as model of reference to simulate metal active site of the catalysts, following the criteria developed elsewhere [24]. All structures including Pd, Pt, Ru and Rh clusters were optimized for triplet spin multiplicity, as the most stable structures, associated with the lowest energies. Frequency calculations were performed on the optimized geometries at the same level of theory, to ensure the systems to be local minima (no imaginary vibration frequencies).

The reaction energy ($\Delta E^{\text{react}}$), enthalpy ($\Delta H^{\text{react}}$) and Gibbs free energy ($\Delta G^{\text{react}}$) for hydrodechlorination of dichloromethane were calculated by using the expressions:

\[ \Delta E^{\text{react}} = \sum E_{\text{products}} - \sum E_{\text{reactants}} \]  \hspace{1cm} \text{Ec. 1}

\[ \Delta H^{\text{react}} = \sum H_{\text{products}} - \sum H_{\text{reactants}} \]  \hspace{1cm} \text{Ec. 2}

\[ \Delta G^{\text{react}} = \sum G_{\text{products}} - \sum G_{\text{reactants}} \]  \hspace{1cm} \text{Ec. 3}
where $E/H/G_{\text{products}}$ and $E/H/G_{\text{reactants}}$ are the absolute electronic energy/enthalpy/Gibbs free energy of isolated (gas phase) products and reactants, respectively.

The stabilization energy of catalytic intermediates ($\Delta E_{\text{interm}}$), adsorbed onto metal cluster ($M_6$), was defined by the expression:

$$\Delta E_{\text{interm}} = E_{\text{metal-intermediate}} - (E_{\text{metal}} + \sum E_{\text{reactants}}) \quad \text{Ec. 4}$$

where $E_{\text{metal}}$ and $E_{\text{reactants}}$ are the electronic energy of isolated $M_6$ cluster and stoichiometric DCM and $H_2$ reactants, and $E_{\text{metal-intermediate}}$ is the total energy of the optimized $M_6$–intermediate system. Hence, a negative $\Delta E_{\text{interm}}$ value indicates an exothermic adsorption process, where the more negative $\Delta E_{\text{interm}}$, the more stable catalytic intermediate.

The desorption energy to obtain the isolated products ($\Delta E_{\text{desorp}}$) was calculated attending the expression:

$$\Delta E_{\text{desorp}} = (E_{\text{metal}} + \sum E_{\text{products}}) - E_{\text{metal-intermediate}} \quad \text{Ec. 5}$$

where $E_{\text{metal}}$ and $E_{\text{products}}$ are the electronic energy of isolated $M_6$ cluster and stoichiometric hydrodechlorination products, and $E_{\text{metal-intermediate}}$ is the total energy of the corresponding $M_6$–intermediate system. Hence, a positive $\Delta E_{\text{desorp}}$ value indicates an endothermic desorption process, where the more positive $\Delta E_{\text{desorp}}$, more heat/higher temperature is required to obtain the final products of DCM hydrodechlorination.

The barrier energy to evolve from different catalytic intermediates ($\Delta E_{\text{barrier}}$) was calculated by the expression:

$$\Delta E_{\text{barrier}} = E_{\text{TS metal-intermediate}} - E_{\text{metal-intermediate}} \quad \text{Ec. 6}$$
where $E_{TS}$ is the electronic energy of the transition state structure between the initial and final $M_6$–intermediates and $E_{metal-intermediate}$ is the total energy of the initial $M_6$–intermediate system.

2.2. Catalysts preparation

The metallic catalysts were prepared by incipient wetness impregnation of a commercial activated carbon (Merck), whose characteristics have been reported elsewhere [31], using acid aqueous solutions (1M) of PtCl$_4$, PdCl$_2$, RhCl$_3$ and RuCl$_3$ (supplied by Sigma-Aldrich) of the required concentrations to obtain 1 wt.% active phase (Pt, Pd, Rh or Ru) nominal loadings. The catalysts were dried overnight at room temperature and heated under air atmosphere to 100 °C at 20 °C h$^{-1}$, the final temperature being maintained for 2 h. The resulted catalysts were called Pt/C, Pd/C, Rh/C and Ru/C.

The final step in the catalysts preparation was their activation, which was carried out by heating them (10 °C min$^{-1}$) up to 250 °C) under a continuous H$_2$ flow (50 Ncm$^3$ min$^{-1}$, supplied by Praxair with a minimum purity of 99.999%), and maintaining these conditions for 2 h.

2.3. Catalysts characterization

The porous structure of the catalysts was characterized by N$_2$ adsorption-desorption at -196 °C (Tristar II 3020, Micromeritics). The samples were previously outgassed for 12 h at 150 °C at a residual pressure of 10$^{-3}$ Torr (VacPrep 061, Micromeritics). The surface areas were calculated by the BET equation.

The X-ray diffraction (XRD) patterns of the catalysts were obtained in a $X'Pert$ PRO Panalytical Diffractometer. The powdered sample was scanned using CuK$\alpha$ monochromatic
radiation (k = 0.15406 nm) and a Ge mono filter. A scanning range of 2θ = 10-100° and a scan step size of 0.0334° with 5s collection time were used.

2.4. Catalytic activity experiments

The HDC experiments were conducted in a continuous flow reaction system described elsewhere [32], consisting of a quartz fixed bed micro-reactor coupled to a gas-chromatograph with a flame ionization detector (FID) to analyze the reaction products. The experiments were performed at atmospheric pressure, with 100 cm³/min of total flow rate, a DCM inlet concentration of 1000 ppmv and 10:1 molar ratio of H₂/DCM. Reaction temperatures of 150-400 °C were tested and a space-time (τ) of 0.8 kg h mol⁻¹ was used in all the experiments.

The behavior of the catalysts was evaluated in terms of DCM and TCM conversion, and selectivity to the different reaction products.

3. Results and Discussion

3.1 Molecular Simulation

Table 1 collects the thermochemical data at 298 K and 1 atm for the hydrodechlorination reaction of dichloromethane to the potential ethylene (C₂H₄), ethane (C₂H₆) and methane (CH₄) products (see Scheme 2) calculated at B3LYP/lanl2dz computational level.

Scheme 2
I: 2CH₂Cl₂ + 2H₂ ⇌ C₂H₄ + 4HCl
II: 2CH₂Cl₂ + 3H₂ ⇌ C₂H₆ + 4HCl
III: 2CH₂Cl₂ + 4H₂ ⇌ 2CH₄ + 4HCl
The values of electronic energy ($\Delta E^{\text{react}}$), enthalpy ($\Delta H^{\text{react}}$) and Gibbs free energy ($\Delta G^{\text{react}}$) of these reactions follow a similar trend at fixed temperature and pressure, describing the hydrodechlorination of dichloromethane as exothermic and spontaneous processes with high equilibrium constants, i.e., a quantitative reactions completely displaced toward products. The reaction thermodynamics is more favorable when increasing the hydrogenation extent in hydrocarbon products; this is, in the order CH$_4$ > C$_2$H$_6$ > C$_2$H$_4$. As exothermic processes, increasing the temperature has the thermodynamic effect of decreasing disfavor?? the conversion of dichloromethane, more significantly in the case of C$_1$ product (CH$_4$) than in the C$_2$ products (C$_2$H$_6$ and C$_2$H$_4$). Reaction energy ($\Delta E^{\text{react}}$) is a thermodynamic parameter independent of pressure and temperature that presents a linear relationship with the standard reaction enthalpy ($\Delta H^{\text{react}}$) (see Figure S1 in Supplementary Material) obtained from formation enthalpy values of reactants and products. For this reason, in the following analysis, we propose using differences in electronic energy to evaluate the stability of reaction intermediates in presence of catalyst ($\Delta E^{\text{int}}$), reaction barriers ($\Delta E^{\text{barrier}}$) and desorption energies ($\Delta E^{\text{desop}}$) for evolving from reactants to intermediates and from intermediates to products, with independence of operating temperature and pressure.

Table 1

The next step in current computational analysis is evaluate the potential catalytic intermediates involved in the hydrodechlorination of dichloromethane by using Pd, Pt, Rh and Ru metal as active specie in the catalyst. As it was already demonstrated [24,25,30], a simple cluster of 6 metallic atoms with triplet spin configuration and charge zero [$M^0_6$ (triplet)] is an adequate molecular model to describe the active species of Pd, Pt, Rh and Ru-based catalysts in the hydrodechlorination of dichloromethane. In this work, new catalytic systems including $M^0_6$
cluster and stoichiometric number of reactants and products (see Scheme 2) were designed by quantum chemical methods. In agreement with previous theoretical results [24,25,30], all Pd₆, Pt₆, Rh₆ and Ru₆ clusters are able to dechlorate one molecule of DCM, obtaining a remarkably stable ••CH₂ radical intermediate linked to two atoms of metal, without significant deformation of M₆ octahedral geometry (Table 1). However, when 2 DCM and 3 H₂ molecules (see Scheme 2) are incorporated in optimization with M₆, only Pd and Rh systems present the stable catalytic intermediates (optimized structures with positive vibrational frequencies) required to evolve toward the desired products (C₂H₄, C₂H₆ and CH₄) (see Figure 1). On the contrary, we were not able to obtain all these stable intermediates using Pt₆ and Ru₆ clusters, what seems to anticipate a lower activity of these later metals in the coupling of chloromethanes.

Figure 1.

Figure 2.

The reaction mechanism described by DFT calculations for the case of Pd catalyst is depicted in Figure 2. Firstly, the structure named “••CH₂-Intermediate” is obtained when dichloromethane and hydrogen molecules interact to Pd₆ or Rh₆ clusters. In this stage, both the dissociation of hydrogen and the dechlorination of DCM occur without barrier of energy, obtaining a very stable structure (see ΔEᵦᵣᵣᵣ chants in Table 2) where each ••CH₂ radical is bonded to two Pd atoms (see Figure 1). The higher stabilization of “••CH₂-Intermediate” in Rh₆ cluster respect to Pd₆ cluster (Table 2) may indicate somewhat higher catalytic activity of rhodium-based catalyst in the HDC of DCM. Arising from “••CH₂-Intermediate”, the system can evolve to new different structures (see Figures 1). Thus, two ••CH₂ radicals can be covalently bonded to obtain “C₂H₄-Intermediate” (Figure 2, left). Then, the hydrogenation process can continue to obtain the “C₂H₆-Intermediate”. Alternatively, the catalytic system can
Evolve differently if a dissociated hydrogen is linked to each ••CH₂ radical to form “•CH₃-Intermediate” (Figure 2, right). From this new intermediate, again two stable structures can be optimized by approaching i) two •CH₃ radicals as alternative pathway to form “C₂H₆-Intermediate”; and ii) the dissociated hydrogens to •CH₃ radicals obtaining “CH₄-Intermediate”. In agreement with the thermochemistry of gas phase reaction, the stability of catalytic intermediates increases with the hydrogenation extent; this is in the order CH₄ > C₂H₆ > C₂H₄ > •CH₃ > ••CH₂ (see ΔE<sub>interm</sub> values in Table 2). On the other hand, the calculated energy barriers to evolve toward the different product intermediates (“C₂H₄-Intermediate”, “C₂H₆-Intermediate” and “CH₄-Intermediate”) are relatively low and close each other (see ΔE<sub>barrier</sub> in Table 3). Finally, the final gas phase products are obtained from the stable catalytic intermediates by applying the required desorption energy, ΔE<sub>desorp</sub> (see Figure 2). Table 3 also collects the calculated desorption energy to generate products for the hydrodechlorination of dichloromethane. As can be observed, desorption energies (ΔE<sub>desorp</sub>) to obtain C₂ and C₁ products are clearly higher than energy barriers (ΔE<sub>barrier</sub>) to evolve between catalytic intermediates. These results would imply a determinant role of the thermodynamics of catalytic intermediates on the process performance. Thus, at the high operating temperatures, the selectivity to C₂ and C₁ is expected to be determined by the stability of both the product intermediates and final products (i.e. ΔE<sub>desorp</sub>) rather than kinetics of the reactions involved.

Considering this hypothesis, quantum-chemical calculations anticipate that the selectivity of palladium-based hydrodechlorination of DCM increases in the order CH₄ > C₂H₆ > C₂H₄.

DFT calculations provide a similar description of the catalytic reaction mechanism for the case of Rh₆ cluster; but it is observed higher stabilization energies (ΔE<sub>interm</sub>) of catalytic intermediates than in Pd₆ based systems (see Table 2), what may indicate a higher catalytic
activity of rhodium-based catalyst. The barriers of energy between the different catalytic intermediates are also higher in Rh₆ than in Pd₆ systems, but again comparatively low respect to stabilization energies and close each other. Significantly, in the case of rhodium catalyst, the obtaining C₂ products requires higher desorption energy than C₁ product, whereas palladium system presents just the opposite behavior (see Table 3). In sum, current computational analysis indicates that Pd may present adequate performance as catalyst for the valorization of chloromethanes by hydrodechlorination process.

Table 2.

Table 3.

3.2. Characterization of the catalysts

All catalysts showed a high BET surface area, with values around 800 m²/g, which appears to be suitable to disperse adequately metal particles on the surface.

Table 4.

The XRD patterns of the fresh-reduced catalysts did not show any remarkable peak associated with zero-valent metal, the main line located at 2θ value of 39.9°, 40.1°, 41.1° and 40.0° for Pt/CM, Pd/CM, Rh/CM and Ru/CM respectively [33]. This suggests that the catalysts are well dispersed as it was found in previous works for similar catalysts [22,31].

3.2. Catalytic activity

3.2.1 Conversion
Figures 4-7 show the conversion of DCM and TCM at different reaction temperatures for all the catalysts, as well as the selectivity to the different reaction products. All the catalysts were very active, reaching almost total conversion with all of them for both reactants at the higher temperatures. Nevertheless, somewhat differences were found in the conversion between the catalysts. When DCM was used as the reactant, Pd/CM and Rh/CM were the most active, at a reaction temperature around 300 ºC the conversion of DCM was total for both catalysts. However, a reaction temperature of 400 ºC was needed to convert DCM totally using Ru/CM while the conversion obtained at this temperature with Pt/CM was 90%. Moreover, as it can be observed in the figures, Pt/CM shows much lower DCM conversion than Ru/CM at lower reaction temperatures. This is in agreement with simulation results where stable intermediates could be formed by adsorption of two molecules of DCM using Pd₆ and Rh₆ clusters, while it was not possible when using Pt₆ and Ru₆. Higher activity of carbon supported Rh and Pd based catalysts was also obtained in studies performed previously with similar catalysts using higher amounts of H₂ [22]. However, in those studies Pt and Ru catalysts showed similar DCM conversion. As can be seen in Figure 4, Pt/CM is very selective to methane even when the proportion of H₂ has been considerably reduced, for this catalyst it seems that reducing H₂ proportion mainly affects to the activity instead to the selectivity which is the case for the other catalysts (Figures 5-7). In accordance with the adsorption energies of reactants [20,34] and the results obtained in previous studies [20,22] the catalysts are considerably more reactive in the HDC of TCM than in the HDC of DCM. In this case, the order of reactivity is the same than that found for similar catalysts and higher proportion of H₂ Pd/CM > Pt/CM > Rh/CM > Ru/CM. The higher reactivity of TCM when comparing to DCM favour the conversion of this compound even in the case that the catalyst is also very selective to methane.
3.2.2. Selectivity patterns

Figure 4 show the selectivity to reaction products for Pt/CM catalyst. As can be seen near total dechlorination of the effluent is obtained, specially for TCM, but only methane is produced. In agreement with molecular simulation results, the intermediates necessary to form hydrocarbons of more than one carbon atoms cannot be stabilized on Pt surface and therefore this is not a suitable catalyst for that purpose.

As can be seen in Figure 5, HDC of both reactants with Ru/CM catalyst leads to very scarce selectivity to hydrocarbons other than methane. The HDC of DCM leads to a high selectivity to methane, the lower value obtained was 70%. The selectivity to ethane was not higher than 20% and 10% of propane. When increasing the reaction temperature the selectivity to monocloromethane decreases, however the selectivity to this compound was not higher than 10% in any case. Beyond 250 °C ethylene is formed and the amount slightly increases with temperature. This can be explained from thermodynamic data of Table 1. As the formation of olefins is less exothermic than that of alkanes, the increase of reaction temperature favors the former. The results are not substantially improved when TCM was used as the reactant as high amounts of DCM or methane are formed. Selectivities to hydrocarbons other than methane up to 30% were obtained. On the other hand, very high temperatures (400 °C) are needed to dechlorinate substantially the contaminant and in this case the main reaction product is by far methane. Nevertheless, it is interesting to note that this catalyst renders mainly ethylene as not chlorinated hydrocarbon different than methane, which is a very interesting compound from an
industrial point of view. Traces of n–butane are observed in both cases. Again, the poor results obtained with this catalyst are in agreement with molecular simulation results as no stable intermediates was possible to form on Ru surface.

Pd/CM is the catalyst which offers the best results in terms of selectivity to non-chlorinated hydrocarbons different than methane for both reactants. Selectivities near 50% were obtained in the hydrodechlorination of DCM and values around 80% when TCM was used. Molecular simulation results demonstrated that formation of intermediates of methane, ethane and ethylene from DCM on Pd surface are very stable ($\Delta E_{\text{interm}} < -140$ kcal/mol), the stability following the order $\text{CH}_4 > \text{C}_2\text{H}_6 > \text{C}_2\text{H}_4$. The same trend was found for the selectivity to these compounds in the HDC of DCM (Figure 6). The higher reactivity of TCM, and the higher amount of H$_2$ needed to dechlorinate the molecule increases the possibility of reaction of adjacent TCM molecules at a similar proportion of H$_2$ which results in a higher selectivity to higher hydrocarbons. Similarly to Ru/CM catalyst, the selectivity to hydrocarbons other than methane increases with reaction temperature. Additionally, the selectivity to olefins is higher when increasing the reaction temperature, specially for the HDC of TCM where at the higher temperature the proportion of ethane and ethylene is similar. This can be explained because of the adsorption energies of the intermediates (Table 2). Rising the temperature benefits the less favored of the intermediates as the desorption energy barriers are very similar in all cases (Table 3). Comparing with the results obtained with Rh/CM, it is evident that this later catalyst shows a lower selectivity to hydrocarbons other than methane than Pd/CM catalyst, despite this metal also has a great capacity to stabilize the intermediates of ethane and ethylene, even higher than Pd (Table 2). Attending computational results, Rh/CM catalyst exhibits a serious drawback for the formation of these hydrocarbons, namely, the energy barriers for their desorption are considerably higher than that of methane (Table 3). In contrast, in the case of Pd, methane,
ethane and ethylene products show similar energy barriers for their desorption from the catalytic surface (Table 3). In the case of Rh/CM catalyst, small amounts of propane were also obtained and traces of butane. Selectivity to C$_1$+, products was around 30% and around 50% for the HDC of chloroform. Similarly to Pd/CM and Ru/CM the selectivity increases with reaction temperature but in this case the effect is less outstanding, the selectivity to chlorinated hydrocarbons diminishes with reaction temperature and the reaction temperature also enhances the selectivity to olefins.

Figure 8 compares the selectivity to non-chlorinated products for all the catalysts. It can be seen that Pt/CM and Pd/CM are very selective to non-chlorinated products regardless if DCM or TCM are used as the reactant products. A similar behavior follow Rh/CM and Ru/CM when DCM is used as the reactant, however the selectivity to chlorinated products considerably increases for the HDC of TCM with these catalysts, specially for Ru/CM. This is in agreement with kinetics results obtained with similar catalyst [35]. In a previous work where a kinetic study of the HDC of DCM and TCM to obtain methane with carbon supported Pd, Pt, Rh and Ru catalysts was performed it was found that Pd/C and Pt/C followed a LHHW model controlled by adsorption. The HDC with Rh and Ru followed the same model but the reaction rate for DCM HDC was controlled by chemical reaction and desorption control was found for the HDC of TCM. The higher desorption energies of HDC products with Rh when compared to Pd (calculated $\Delta E^{desorp}$ data in Table 3) is consistent with a stronger difficulty for the formation of hydrocarbons. In fact, the amount of non-chlorinated products increases with reaction temperature, which is very evident in the case of Ru catalyst (Figure 5).
It can be concluded that Pd, and particularly carbon supported Pd catalysts, appear to be promising catalysts for the obtaining of C₂ hydrocarbons from chloromethanes dechlorination. Rh carbon supported catalysts shows lower yields but is more prone to the production of C₃ hydrocarbons. Further optimization of the catalyst and the operating conditions will be needed which will permit better yields to the desired products.

4. Conclusions

Carbon supported Pd catalysts are promising systems for the valorization of chloromethanes to obtain ethane and ethylene. Stable catalytic intermediates were obtained by computational analysis in the hydrodechlorination of DCM on Pd and Rh clusters, presenting ••CH₂ and •CH₃ radicals and C₂H₄, C₂H₆ and CH₄ products. On the contrary, it was not possible to obtain all these stable intermediates using Pt₆ and Ru₆ clusters. Rh₆ cluster presents somewhat higher stabilization energies than Pd₆ based systems, however, the barriers of energy between the different catalytic intermediates are higher in Rh₆ than in Pd₆, as well as the desorption energies of C₂ products which hinders their formation. In agreement with the thermochemistry of gas phase reaction, the stability of catalytic intermediates increases with the hydrogenation extent; this is in the order CH₄ > C₂H₆ > C₂H₄ > •CH₃ > ••CH₂. It should be remarked that the stability order of catalytic intermediates agrees with the experimental selectivity of the hydrodechlorination of DCM, what seems to indicate a determinant role of the thermodynamics of catalytic intermediates on the process performance. In agreement with computational results, the Pd based catalyst showed the best performance for the valorization of chloromethanes by hydrodechlorination to obtain C₂ products. Yields near 50% were obtained in the HDC of DCM and higher than 70% in that of TCM. It is followed by Rh, Ru and Pt which shows almost no selectivity to C₂ products. The selectivity to C₂ products increases with the temperature with a higher proportion of ethylene.
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References


### Tables

Table 1. Reaction energy ($\Delta E^{\text{react}}$), enthalpy ($\Delta H^{\text{react}}$) and Gibbs free energy ($\Delta G^{\text{react}}$) for hydrodechlorination of dichloromethane to form ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$) and methane (CH$_4$), calculated at B3LYP/lanl2dz computational level

<table>
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<tr>
<td></td>
<td>-17.6</td>
<td>-18.6</td>
<td>-30.9</td>
<td>-59.2</td>
</tr>
</tbody>
</table>

Table 2. Stabilization energy of catalytic intermediates ($\Delta E^{\text{interm}}$) for hydrodechlorination of dichloromethane to form ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$) and methane (C$_2$H$_4$), calculated at B3LYP/lanl2dz computational level

| Catalyst Cluster | $\Delta E^{\text{interm}}$ (kcal/mol) | | | |
|---|---|---|---|---|---|---|
| Pd$_6^0$ (Triplet) | | | | | | |
| $\bullet$CH$_2$- Intermediate | -97.8 | | | | | |
| C$_2$H$_4$- Intermediate | -140.9 | | | | | |
| $\bullet$CH$_3$- Intermediate | -157.4 | | | | | |
| C$_2$H$_6$- Intermediate | -180.7 | | | | | |
| CH$_4$- Intermediate | -212.1 | | | | | |
| Rh$_6^0$ (Triplet) | | | | | | |
| $\bullet$CH$_2$- Intermediate | -187.6 | | | | | |
| C$_2$H$_4$- Intermediate | -181.1 | | | | | |
| $\bullet$CH$_3$- Intermediate | -194.1 | | | | | |
| C$_2$H$_6$- Intermediate | -211.4 | | | | | |
| CH$_4$- Intermediate | -222.5 | | | | | |
Table 3. Barrier of energy to generate the catalytic intermediates ($\Delta E_{\text{barrier}}$) and desorption energy to generate products ($\Delta E_{\text{desorp}}$) for the hydrodechlorination of dichloromethane, calculated at B3LYP/lanl2dz computational level.

<table>
<thead>
<tr>
<th>Catalyst Cluster</th>
<th>$\Delta E_{\text{barrier}}$ (kcal/mol)</th>
<th>$\Delta E_{\text{desorp}}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_2H_4$ - Intermediate</td>
<td>$\bullet CH_3$ - Intermediate</td>
</tr>
<tr>
<td>$Pd_6^\circ$(Triplet)</td>
<td>18.3</td>
<td>14.4</td>
</tr>
<tr>
<td>$Rh_6^\circ$(Triplet)</td>
<td>31.8</td>
<td>34.5</td>
</tr>
</tbody>
</table>

Table 4. BET Surface area of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>777</td>
</tr>
<tr>
<td>Rh/C</td>
<td>855</td>
</tr>
<tr>
<td>Ru/C</td>
<td>796</td>
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<tr>
<td>Pt/C</td>
<td>870</td>
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</tbody>
</table>
Figure 1. Optimized structures of catalytic intermediates obtained by quantum-chemical calculations at B3LYP/lanl2dz computational level with Pd
Figure 2. Scheme of reaction mechanism for hydrodechlorination of dichloromethane obtained by quantum-chemical calculations at B3LYP/lanl2dz computational level for Pd
Figure 3: XRD patterns of Ru, Rh, Pt and Pd catalysts after a reduction in H\textsubscript{2} at 250\degree C.
Figure 4. Effect of temperature on conversion and selectivity with Pt/CM catalyst. (a) HDC of DCM; (b) HDC of TCM. Products and byproducts: CH₄ (●), C₂H₆ (+), C₂H₄ (-), C₃H₈ (★), C₃H₆ (◇), MCM (■), C₄H₈ (×), n-C₄H₁₀ (□), DCM (▲), XDCM/TCM (♦)
Figure 5. Effect of temperature on conversion and selectivity with Ru/CM catalyst. (a) HDC of DCM; (b) HDC of TCM. Products and byproducts: CH$_4$ (●), C$_2$H$_6$ (+), C$_2$H$_4$ (-), C$_3$H$_8$ (☆), C$_3$H$_6$ (◇), MCM (■), C$_4$H$_8$ (×), n-C$_4$H$_{10}$ (□), DCM (▲), XDCM/TCM (●)
Figure 6. Effect of temperature on conversion and selectivity with Pd/CM catalyst. (a) HDC of DCM; (b) HDC of TCM. Products and byproducts: CH\textsubscript{4} (●), C\textsubscript{2}H\textsubscript{6} (+), C\textsubscript{2}H\textsubscript{4} (−), C\textsubscript{3}H\textsubscript{8} (*), C\textsubscript{3}H\textsubscript{6} (◇), MCM (■), C\textsubscript{4}H\textsubscript{8} (几十), n-C\textsubscript{4}H\textsubscript{10} (□), DCM (▲), XDCM/TCM (●)
Figure 7. Effect of temperature on conversion and selectivity with Rh/CM catalyst. (a) HDC of DCM; (b) HDC of TCM. Products and byproducts: CH₄ (●), C₂H₆ (+), C₂H₄ (-), C₃H₈ (×), C₃H₆ (◇), MCM (■), C₄H₈ (×), n-C₄H₁₀ (□), DCM (▲), XDCM/TCM (♦)
Figure 8. Selectivity to non-chlorinated products with the catalysts (Pd/CM, Rh/CM, Ru/CM and Pt/CM); at different temperature with DCM and TCM.