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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 $\cdot\cdot CH_2$ and $\cdot CH_3$ radicals and C_2H_4, C_2H_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 °C. 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.

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 quantities of residual chloromethanes is not so abundant to be considered an alternative source of hydrocarbons to natural gas or oil, although their valorization is of high interest. 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

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$$CH_3Cl \rightarrow 1/2\ C_2H_4 + HCl$$

$$CH_4 + HCl + 1/2O_2 \rightarrow CH_3Cl + H_2O$$

Scheme 1. Alternative route for olefins production based on the dechlorination of monochloromethane.

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.

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 dichoromethane (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]. In the chlorination of methane, the first product formed is chloromethane, CH_3Cl. If enough chlorine is present, further substitution may occur, forming dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and finally carbon tetrachloride (CCl_4). These compounds could be further hydrodechlorinated with the proper catalysts to modulate the selectivity in order to obtain C2 + hydrocarbons. With this alternative, hydrodechlorination of chloromethanes (previously obtained from methane chlorination) would be considered a potential source of hydrocarbons. Other inconveniences found in these studies, which use catalytic materials like ZSM-5, HZSM-5, SAPO-34 or HSAPO-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. Furthermore, without forgetting that the principal purpose of the hydrodechlorination of chloromethanes is reduce toxicity, the increase of the selectivity of the process to C2 or C3 hydrocarbons instead of methane, results in a reduction of the hydrogen consumption adding an economic advantage to the process. 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 choloromethanes.

The aim of this work is to evaluate the ability of different metals

$$\text{I: } 2CH_2Cl_2 + 2H_2 \leftrightarrows C_2H_4 + 4HCl$$

$$\text{II: } 2CH_2Cl_2 + 3H_2 \leftrightarrows C_2H_6 + 4HCl$$

$$\text{III: } 2CH_2Cl_2 + 4H_2 \leftrightarrows 2CH_4 + 4HCl$$

Scheme 2. Hydrodechlorination reactions of dichloromethane to ethylene, ethane and methane.

(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 C_2 and C_3 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 (M_6). 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 C_2 and C_3 hydrocarbons. Higher reaction temperatures (up to 400 °C) 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

Table 1
Reaction energy (ΔE^{react}), enthalpy (ΔH^{react}) and Gibbs free energy (ΔG^{react}) for hydrodechlorination of dichloromethane to form ethylene (C_2H_4), ethane (C_2H_6) and methane (CH_4), calculated at B3LYP/lanl2dz computational level.

Reactants	Products								
CH_2Cl_2, H_2	C_2H_4			C_2H_6			CH_4		
kcal/mol									
	ΔE^{react}	ΔH^{react}	ΔG^{react}	ΔE^{react}	ΔH^{react}	ΔG^{react}	ΔE^{react}	ΔH^{react}	ΔG^{react}
	−17.6	−18.6	−30.9	−59.2	−53.3	−57.3	−81.6	−72.6	−79.4

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