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A theoretical analysis of the molecular events involved in hydrocarbons reactivity on palladium clusters

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Palladium clusters have been chosen to represent a nanosized catalyst apt for a theoretical study on some fundamental aspects of surface molecular events. The investigation has been focused on hydrocarbon transformations to give dehydrogenation and hydrogenolysis products. The energetic details of the involved elementary processes have been calculated through density functional theory (DFT). The Becke Lee–Yang–Parr hybrid (B3LYP) functional was adopted to calculate exchange and correlation energy. An effective core potential basis set (ECP on core electrons and Dunning/Huzinaga on outer electrons) was found sufficiently accurate to reproduce experimental data. Clusters containing up to seven Pd atoms were considered and their interaction with hydrogen, methane and ethane and their fragments was analyzed and a kinetic study of the system was performed. Transition states structures and energies were calculated through quantum mechanics and the corresponding kinetic constants were derived from a statistic thermodynamic approach. On the basis of such information, a kinetic model that accounts for ethane transformations has been formulated. The scaling of such an atomic scale information to reactor scale is also considered.

Keywords: Density functional theory; Catalysis; Palladium; Cluster; Kinetics; Ethane; Ethylene

1. Introduction

Supported palladium plays a leading role as a catalyst, particularly in hydrocarbon transformations such as in hydrogenation and hydrocracking processes. This aptitude is partially due to its peculiar power to absorb hydrogen [1]. One of the key factors influencing the properties and performances of supported metal catalysts is the metal particle size, which is directly connected with the amount of active sites present on the catalytic surface. In fact, a variation in the dimension of the aggregates deposited on the support induces a change in number and coordination state, thus also in electronic configuration, of surface atoms. Thanks to the increase in computer speed, in these last years quantum chemistry calculations can be profitably employed in order to deepen the mechanisms of the elementary events involved in the mentioned catalytic processes. The relevance of this approach is at the present strengthened by the possibility of coupling the obtained information with the available sophisticated characterization techniques [2].

In the present paper the results of a theoretical study on the transformations of simple hydrocarbons on isolated palladium clusters are reported and discussed.

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Despite the simplification of considering isolated clusters and then neglecting the influence of the support, some interesting results can be obtained on the catalytic role of nanosized particles possessing intermediate properties between isolated atoms and the bulk solid. Particularly, the investigation was focused on the identification of the most important elementary processes that occur when hydrogen or an hydrocarbon gas phase molecule interact with one or more Pd surface atoms. Structures and energies of isolated palladium clusters and of palladium-adsorbed hydrocarbon systems were calculated in a preceding work [3] and have been used here to develop a kinetic scheme for the catalytic reactions of C_2 hydrocarbons with hydrogen. The latter was then employed to investigate the evolution with reactor residence time of the chemical species involved in the process. Because no published data of ethane hydrogenation over palladium clusters were found in the literature, neither on palladium single crystals, the main outcome of this work was the formulation of a “toy model” aimed to the deepening of the mechanistic details of the elementary steps involved in the process under investigation. Obviously, the model needs to be tested experimentally but, at the same time, it will guide the design of a tailored experimental campaign.

2. Theory

In this work, structure and energy of all the considered species were calculated through density functional theory (DFT), that has the advantage over other ab initio methods of scaling by the square or cube of the problem size. Exchange and correlation energy were calculated with the three parameter Becke Lee–Yang–Parr hybrid (B3LYP) functionals [4,5]. The chemical inert core orbitals of palladium were described with the effective core potentials of Hay and Wadt [6,7], which include relativistic effects on valence electrons, while the external orbitals were represented with a double-ζ basis set [8]; Dunning/Huzinaga full double-ζ basis set was adopted for hydrogen and carbon atoms (Lanl2DZ) [9]. The calculation method was validated by comparison with other combinations of functionals and basis sets in the estimation of Pd–Pd and Pd–H bond strengths [3], giving a good agreement with experimental data. All the calculations were performed with the Gaussian 98 program suite [10].

The strategy used to study the structures of the Pd clusters here considered consisted in hypothesizing different starting geometries, which were optimized adopting the Berny algorithm and redundant internal coordinates. The stability of these structures was verified computing the force constant and vibrational frequencies: an optimized structure was considered stable when possessing no imaginary vibrational frequencies.

3. Results and discussion

3.1. Cluster structures and related energetic features

It is advisable to recall some significant features obtained on the structures and the energies of palladium clusters and their interaction with hydrogen and hydrocarbons [3].

The calculated structures of Pd_n clusters correspond to almost regular polyhedrons, all stable as triplets. Increasing n, the dependence of energy on cluster size decreases and species progressively tends to the bulk solid. On the contrary, Pd_n–H clusters are all stable as doublets and with $n \geq 3$ the hydrogen atom is threefold coordinated. With $n \geq 4$ an almost constant value of the bond strength, equal to about 61.0 kcal mol^{-1}, was calculated. The whole behavior of the Pd–H bond strength is illustrated in Fig. 1.

Repeating the study for the Pd_n–CH_x Pd clusters, with $x = 1$–3, it was found that increasing the number of hydrogen atoms of the hydrocarbon moiety the coordination number of carbon atom decreases and the Pd–C bond length increases, while the palladium clusters substantially maintain their regular structure. Finally, it is interesting to observe that the insertion of C within Pd_n clusters occurs when no H atoms are bonded to C.

Considering the asymptotic behavior of bond strengths illustrated in Fig. 1, in the following, Pd_6 was chosen as a representative of a Pd cluster to analyze the system reactivity. Particularly, in Fig. 2, the optimized structures of methane fragments with Pd_6 cluster and the schematic representation of methane dissociative adsorption are illustrated.

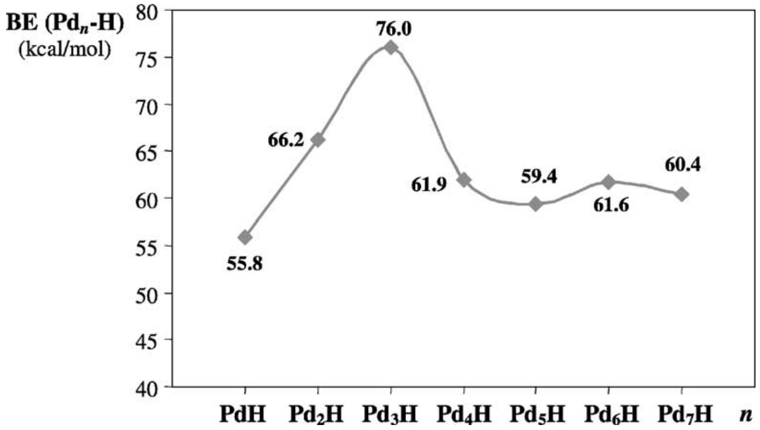

Fig. 1. Palladium–hydrogen bond energies (kcal mol^{-1}) in Pd_nH clusters as a function of cluster size ($n = 2$–7).

3.2. *Reactions of ethane with hydrogen*

As already mentioned, in order to explore the catalytic action of Pd clusters with respect the reaction of ethane with hydrogen, both the dehydrogenation and hydrogenolysis reactions were considered:

Dehydrogenation $CH_3–CH_3 \rightarrow CH_2{=}CH_2 + H_2$

Hydrogenolysis $CH_3–CH_3 + H_2 \rightarrow 2CH_4$

The attention was devoted on the influence of temperature, pressure, amount of hydrogen $n^0_{H_2}$ and conversion ξ on selectivity S, defined as follows:

$$S = \frac{\text{moles of } C_2H_4}{\text{moles of } CH_4} = f(T, P, n^0_{H_2}, \xi) \qquad (1)$$

The proposed detailed kinetic scheme is summarized in Table 1. It consists of 12 elementary surface reactions, that can be divided into two main groups: adsorption and desorption reactions and reactions

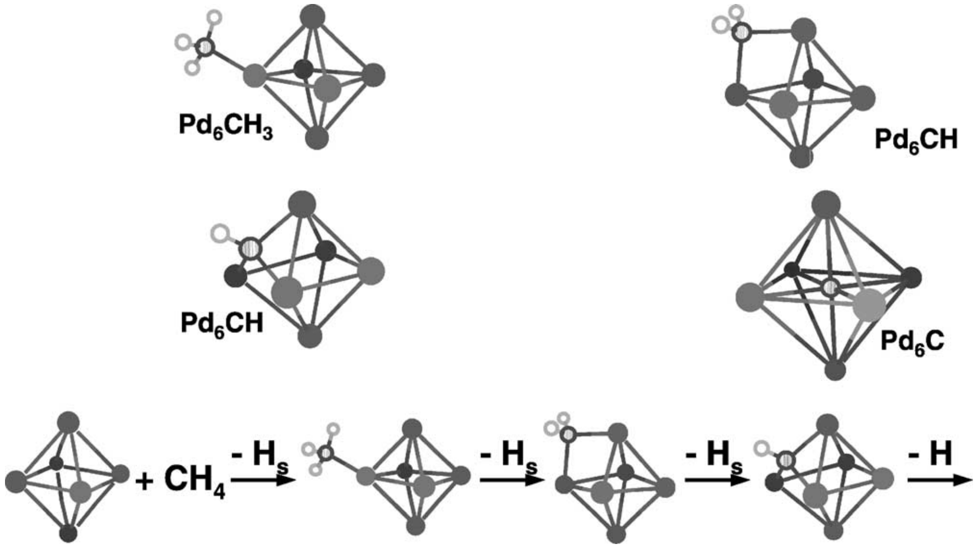

Fig. 2. Example of the interaction of Pd_6 cluster with methane fragments and of its dissociative adsorption (up to C incorporation within the cluster).

Table 1
Mechanism proposed for ethane reactions with hydrogen and relative kinetic parameters

		log A	α	E_{act}
(R1)	$C_2H_6 + \sigma \rightarrow C_2H_5^* + H^*$	20.7	0.5	6030
(R2)	$C_2H_5^* + \sigma \rightarrow C_2H_4^* + H^*$	22.3	0.0	15100
(R3)	$C_2H_4^* \rightarrow C_2H_4 + \sigma$	17.63	−0.5	18390
(R4)	$C_2H_5^* + \sigma \rightarrow CH_2^* + CH_3^*$	23.31	0.0	29000
(R5)	$CH_2^* + H^* \rightarrow CH_3^* + \sigma$	23.00	0.0	0
(R6)	$CH_3^* + H^* \rightarrow CH_4 + 2\sigma$	26.26	0.0	0
(R7)	$2H^* \rightarrow H_2 + 2\sigma$	22.89	0.0	9000
(R8)	$C_2H_4 + \sigma \rightarrow C_2H_4^*$	11.78	0.5	0
(R9)	$H_2 + 2\sigma \rightarrow 2H^*$	18.02	1.0	0
(R10)	$CH_4 + 2\sigma \rightarrow CH_3^* + H^*$	20.85	0.5	10000
(R11)	$C_2H_5^* + H^* \rightarrow C_2H_6 + \sigma$	26.6	−0.5	0
(R12)	$C_2H_4^* + H^* \rightarrow C_2H_5^* + \sigma$	22.94	0.0	27390

The value of k is expressed as $AT^{\alpha}\exp(-E_{act}/RT)$ in units consistent with cal, cm^3, s, K, mol. The superscript asterisk (∗) indicates an adsorbed species and σ represents a free surface site.

between adsorbed species. A dissociative adsorption of ethane (R1) and hydrogen (R9) was assumed, in agreement with mechanisms proposed by Sinfelt [11], and Cimino et al. [12]. The adsorbed ethyl can loose another hydrogen leading to adsorbed ethylene (R2) which successively desorbs (R3), or it can split into the methyl and methylene moieties (R4) which can react with adsorbed hydrogen to form methane (R5 and R6). Ethylene adsorption has been considered single site, as palladium shows a well-established propensity toward the formation of π-olefinic adspecies [13]. The proposed scheme is consistent with a detailed analysis where all the energetic features of the surface reactions are considered. The mentioned energetic behavior is depicted in Fig. 3, where the relative levels of any of the intermediate species involved in the proposed mechanism is reported.

3.3. Evaluation of reaction rate parameters

The reaction rate constants for the different elementary reactions summarized in Table 1 were expressed by means of the following Arrhenius like equation as a function of three parameters A, α and E_{act}:

$$k = AT^{\alpha}\exp\left(-\frac{E_{act}}{RT}\right) \tag{2}$$

The values for the hydrocarbon adsorption reactions (R1), (R8) and (R10) were evaluated from the collisional theory and were equated to the probability of a gas molecule to hit a surface, assuming, in the absence of experimental or theoretical data, a unitary sticking coefficient. The determination of kinetic constants for the two surface reactions (R2) and (R4) was performed through transition state theory, locating the transition state using the synchronous transit-guided quasi-Newton method [14]. Selected geometrical parameters of the calculated transition state structures for a Pd cluster of six atoms are reported in Fig. 4. Each transition states, indicated in the following symbol ≠, was characterized by the presence of a single negative vibrational frequency. Transition state theory requires knowledge of the partition function of the molecule in the transition state and of the reactants according to the equation:

$$k = s_F\frac{k_B T}{h}\frac{Q_{vib}^{\neq}}{Q_{vib}^{react}}\exp\left(-\frac{E_{act}}{RT}\right) \tag{3}$$

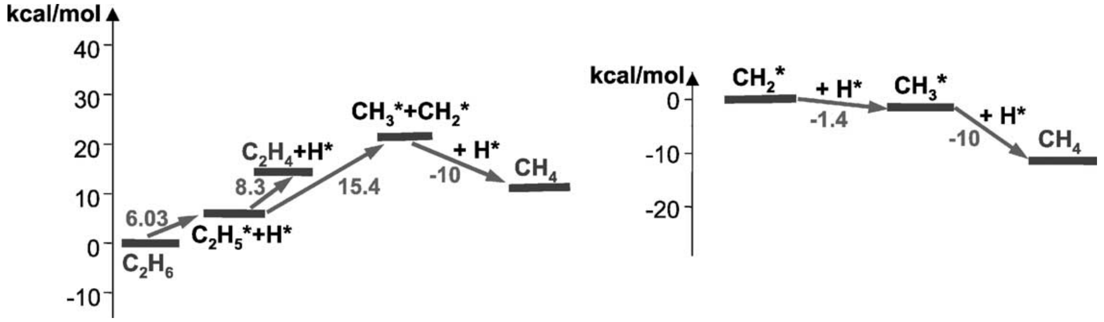

Fig. 3. Sketch of the energetics of surface reactions for ethane and hydrogen reacting on a Pd_6 cluster. Bold species are in the gas phase while the superscript asterisk (∗) designates adsorbed species. Energy differences, in kcal mol^{-1}, are evidenced.

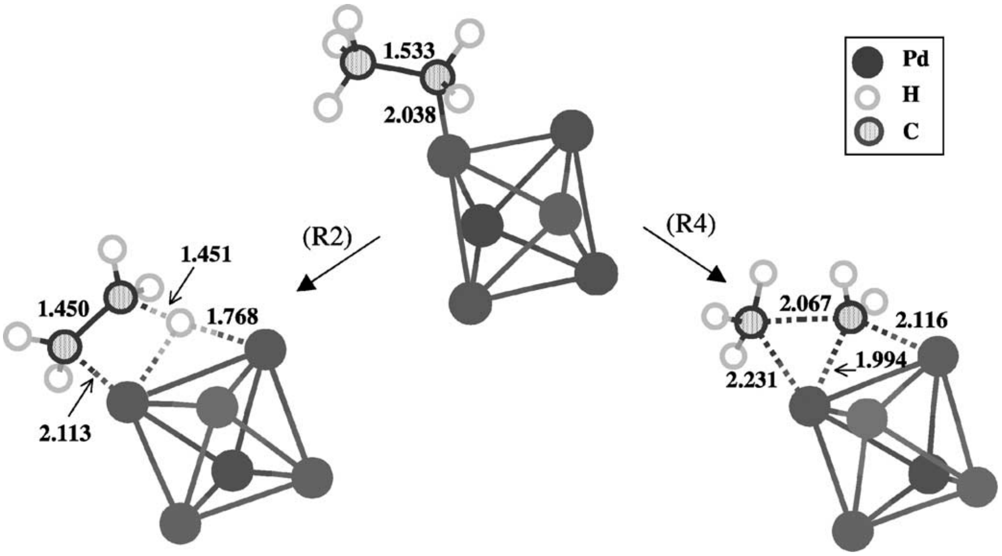

Fig. 4. Structure of transition states for reactions (R2) and (R4) over a Pd_6 cluster, as determined through quantum chemistry calculations. Distances are reported in Å.

where s_F is the number of equivalent paths, k_B and h the Boltzmann and Plank constants, T the temperature, E_{act} the activation energy of the process, and $Q_{vib}^{\neq}$ and Q_{vib}^{react} are the vibrational partition functions of the transition state and of the reactants, respectively. Implicit in expression (3) is the omission of translational, rotational and electronic partition functions, which equals the consideration that adsorbed surface species have no translational and rotational degrees of freedom.

Fig. 5 shows the transition state structures for clusters of three, four and six Pd atoms, together with the calculated activation energies and pre-exponential factors. It can be noticed that kinetic parameters calculated for reactions on Pd_3 are quite different from those derived for bigger clusters, although its structure could represent the bigger cluster face involved in the process. This behavior can be attributed to the very high bond strengths calculated between Pd_3 and adsorbed hydrocarbons or hydrogen. Kinetic parameters for reactions on Pd_4 are more similar to those calculated on Pd_6 (i.e. those introduced in the kinetic scheme to simulate the system behavior) but still different. This discrepancy is probably due to a different disposability of palladium atoms to coordinate the adsorbed molecules.

Reaction (R5) was supposed to be fast and with no activation energy. For hydrogen desorption (R9) the frequency factor was assumed as that experimentally determined on a Pd(1 1 1) surface [15] and the activation energy was calculated through transition state theory for hydrogen desorption on a Pd_6 catalyst.

Finally, the kinetic constants of the remaining reactions, which are all backward reactions of those already mentioned, were calculated applying the thermodynamic consistency. The numerical values of the kinetic parameters of all the elementary reaction involved in the proposed reaction path are summarized in Table 1.

3.4. Kinetic behavior of the system

A preliminary study of the behavior of the reaction system under investigation was performed under the set of the following simplifying hypothesis:

- pseudo-stationary hypothesis was assumed to evaluate the adsorbed species concentrations;
- accordingly with the available thermodynamic data, only the dehydrogenation reaction is significantly limited by equilibrium conditions;

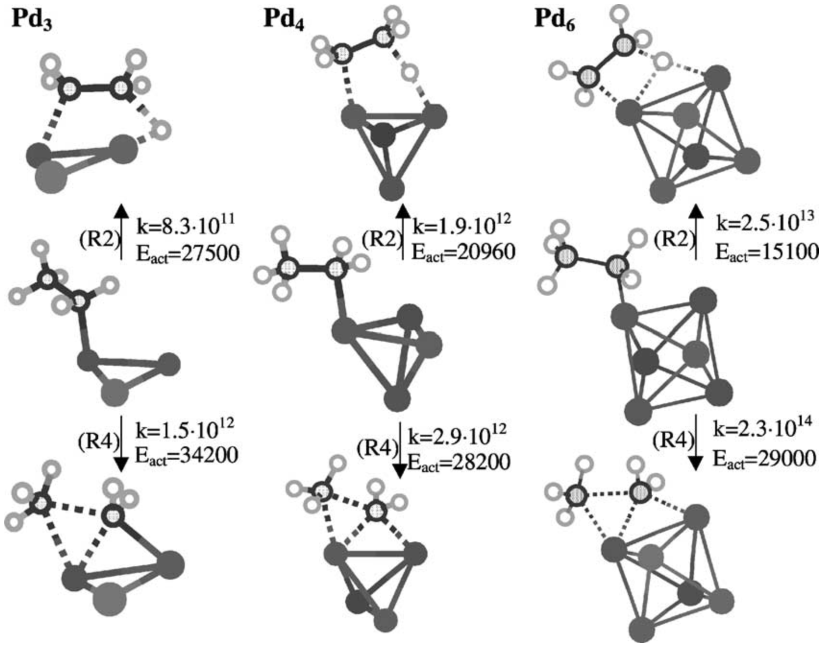

Fig. 5. Structure of transition states for reactions (R2) and (R4) over Pd_3, Pd_4 and Pd_6 clusters, as determined through quantum chemistry calculations. In the picture gray atoms represent Pd, white atoms H and dotted ones C. For each reaction the pre-exponential factor (s^{-1}) and the activation energy (cal mol^{-1}) are indicated.

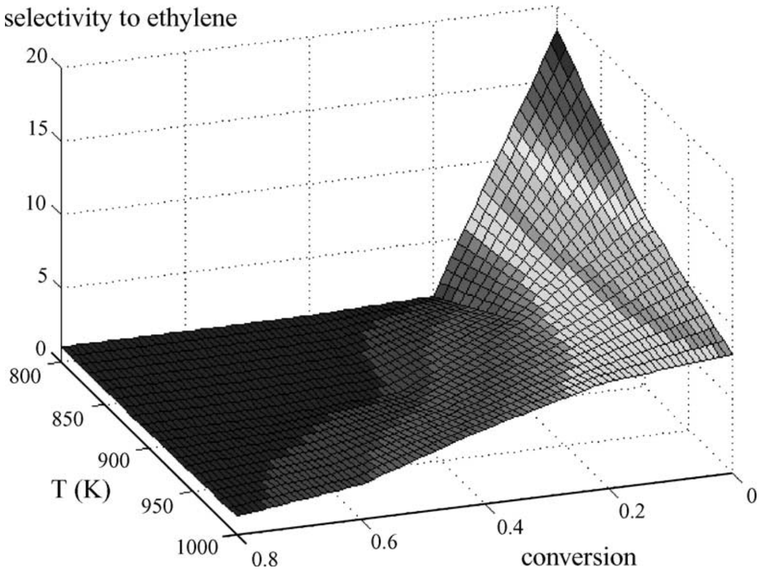

Fig. 6. Surface representing the relationship among temperature, conversion and selectivity for the ethane/H_2 reaction on Pd clusters.

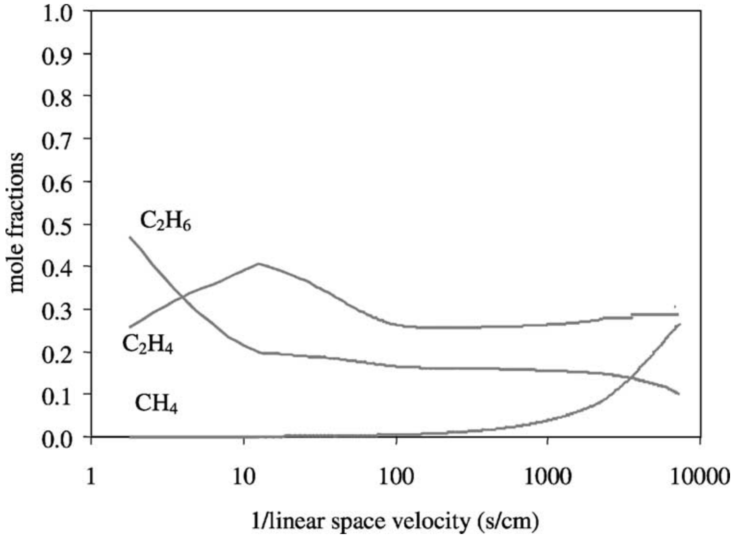

Fig. 7. Mole fractions of reaction products at 753 K and atmospheric pressure as a function of the inverse of linear space velocity ($s\,cm^{-1}$), as calculated through the heterogeneous-PFR model (feed mole ratio C_2H_6:H_2 = 49).

- following the energy schemes of Fig. 3, the significant rate processes are assumed to be:

$$C_2H_5^* \rightarrow C_2H_4 + H^*$$

$$C_2H_5^* \rightarrow CH_2^* + CH_3^*$$

The previous analysis brought to the diagram of Fig. 6, where the relationship among temperature, conversion and selectivity is depicted.

The detailed kinetic behavior of the system was tested by embedding the whole kinetic scheme into a heterogeneous plug flow reactor model. Palladium clusters were assumed to be deposited on a silicon surface and the number of palladium active sites was chosen, for sake of simplicity, equal to that of silicon. The calculated gas phase mole fractions of the most important chemical species as a function of the linear space velocity are reported in Fig. 7, where the considered conditions refer to a reactor working at 753 K and atmospheric pressure and with a ethane/hydrogen feed mole ratio equal to 49. By the inspection of the figure, it can be seen that at low values of residence time the process exhibit a high selectivity to ethylene, which is the kinetically favored product, as results from a comparison between activation energies of reactions (R2) and (R4), while at longer times the thermodynamic aspect prevails, leading to the formation of methane.

4. Conclusions

The elementary steps involved in the reaction of ethane with hydrogen over palladium was studied through quantum chemistry calculations; palladium clusters, in particular Pd_6, were assumed as a simplification of a generic supported palladium catalyst. A kinetic scheme was derived which provides dissociative adsorption of reactants, surface reactions among adsorbed species, which leads to the two products ethylene, coming from ethane dehydrogenation, and methane, deriving from ethane hydrocracking, and desorption of products. Kinetic constants were calculated through transition state or collisional theory for surface and adsorption reactions, respectively.

The influence of cluster dimension on kinetic constants was then investigated. It was found that, although transition state structures are quite similar, the kinetic parameters can significantly differ. This is probably determined by the change of the strength with which palladium atoms coordinate adsorbed species, which varies progressively with increasing cluster size.

The kinetic scheme was then embedded in a heterogeneous plug flow reactor model in order to investigate the formation of the principal products. For low residence times the kinetically favored product, ethylene, prevails, while for longer times the reaction leads to the formation of methane, which is thermodynamically favored.

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