Development and characterization of ZnO, Au/ZnO and Pd/ZnO thin films through their adsorptive and catalytic properties

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Abstract

In this paper, we report (a) the development of ZnO thin films prepared by pulsed laser deposition and partially covered with nano-particles Pd or Au and (b) their physicochemical study, in order to investigate their catalytic and/or adsorptive properties. It is the first time where two different and popular methods, namely pulsed laser deposition and reversed flow-inverse gas chromatography, are combined. The inverse gas chromatographic technique with the corresponding time-resolved analysis is used for the first time in order to characterise compounds in the nano-scale domain. We focus on the determination of physicochemical quantities mainly concerning the adsorption in thin films, with (Pd/ZnO) or without (Au/ZnO) catalytic behaviour. Thus, entropy and other important physicochemical quantities are calculated which reveal the mechanism of adsorption as well as of isomerization–hydrogenation of 1-butene and contribute to the study of heterogeneity of thin film surfaces. The programs used have been written in Fortran. An important achievement is also the determination of the standard deviations of the kinetic constants.

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1. Introduction

Metal oxides thin film structures have attracted the attention of many users and scientists interested in catalytic activity and especially in gas sensing applications. In particular, ZnO has been extensively studied during the last years because of its large variety of applications. Many techniques like sputtering [1], chemical vapor deposition (CVD) [2] and other evaporation methods [3] were applied to grow the ZnO thin films. Pulsed laser deposition (PLD) provides a unique means of deposition relying on its simplicity, versatility, and stoichiometry transfer of the target to the film and low processing temperature, without a corrosive gas presence, crucible and evaporation cell. Especially, the laser ablated species possess relatively high kinetic energy (10–100 eV), forming epitaxial or textured growth at low temperatures [4].

Promoters in the form of metal clusters on the top [5] or inside [6] ZnO thin films were also deposited and investigated to improve their structural, optical and electrical characteristics. Not many works involve real time analysis of the interactions between the surface and the surrounding gases [7,8]. Pure theoretical approaches made for the determination of quantities as fractional coverage or adsorption sites [9,10] exist, as well as in combination with experimental measurements [11–14].

On the other hand, adsorption isotherms and surface energy distribution functions on heterogeneous surfaces have been the subject of many efforts during the last two decades for characterizing heterogeneous solids by calculating adsorption energy distribution functions from retention volume data. All these works offer approximate functions or values through approximate solutions without any determination of the actual values of adsorption parameters.

Of all the classical methods for measuring adsorption energies, isotherms, etc. none has led to local values. Difficulties like these led scientists to turn to numerical solutions [15,16].

Reversed flow-inverse gas chromatography (RF-IGC) offers many possibilities for physicochemical measurements, as rate
and distribution constants, experimental isotherms, deposition velocities and reaction probabilities, mass transfer coefficients, all pertaining to the mechanism of homogeneous and/or heterogeneous reactions [17–20]. In the mean time, the RF-IGC method has been expanded and is adequate for adsorption parameter calculations, as local adsorption isotherms, local monolayer capacities, probability density functions for adsorption energies and energies from lateral interactions [21]. Thus, the RF-IGC method is applied to create and provide a new pathway for solids characterization [22–24].

RF-IGC is also a dynamic method useful for measuring adsorption isotherms at low concentrations. This method, based on the mass-balance equations, is useful for evaluating the adsorption isotherms because it gives model-independent results. Thus, one can conclude safely and accurately concerning chemical reactivity and kinetics and give correct explanations for the systems examined. The reason is that kinetic parameters are closely related to the existing adsorption isotherm, depending strongly on the adsorption–desorption phenomena.

In this paper, we report the study of ZnO thin films, prepared by PLD and partially covered with Pd or Au, in respect to the hydrogenation of 1-butene in order to investigate their adsorptive and catalytic properties. We focus on the determination of physicochemical quantities mainly concerning the adsorption in thin films, with (Pd/ZnO) or without (Au/ZnO) catalytic behaviour.

Such a study was conducted for the first time, to our knowledge, using RF-IGC, by inserting the thin film deposited on a glass rod substrate directly into the GC column. In particular, we investigated the adsorption occurring on gas–solid interfaces, where the solids are heterogeneous in nature with dimensions in the nano-scale domain, as well as the catalytic behaviour in the isomerization–hydrogenation reactions of 1-butene.

2. Experimental

2.1. Development of thin films by PLD

2.1.1. Materials

The materials which have been used for the development of thin films are ZnO (99.998%), O₂ (99.998%), metals Pd, Au (Alfa Aesar, 99.9%).

2.1.2. Procedure

The thin film deposition was performed inside a stainless steel vacuum chamber evacuated down to a residual pressure of about $10^{-4}$ Pa prior to each irradiation (cf. Fig. 1). ZnO thin films were first deposited from a 99.998% pure ZnO target using an ArF* (193 nm) excimer laser. The target for the host material was at room temperature and the pressure inside the chamber was kept at 20 Pa, under flow of pure oxygen (99.999%). Subsequently, a Pd or Au target was ablated under vacuum ($2 \times 10^{-4}$ Pa) and different ZnO surface coverage resulted by changing the deposition time. To avoid fast drilling, all targets were placed on a vacuum compatible, computer-controlled XY stage synchronized with the pulsed laser. The deposition time was 120 min for the ZnO thin film and 8 and 2 min for the metal clusters Pd and Au, respectively. The laser fluence and the frequency (3 J/cm² at 10 Hz) were kept constant during the ablation of all targets. The substrates were glass rods, 50 mm long and 3 mm thick, selected to fit into the GC column and were kept at room temperature during each deposition. Special developed holders were positioned 50 mm parallel to the target’s surface and rotated by vacuum compatible motors to achieve a homogeneous thin film area. For comparison reasons, two identical ZnO thin films were deposited simultaneously. Then one of them was removed and the other subsequently partially covered by the Au or Pd clusters.

2.2. Physicochemical study

2.2.1. Materials

The materials which have been used for the determination of catalytic and/or adsorptive properties of thin films are 1-butene (99,999%), H₂ (99,999%), thin films of ZnO, Au/ZnO, Pd/ZnO. The gases have been supplied from Air Liquide, Greece.

2.2.2. Procedure

The RF-IGC method involves a flow-rate perturbation of the carrier gas which is achieved experimentally simply by using a four- or six-port gas sampling valve and reversing the direction of flow of the carrier gas, usually for a short time interval. If pure carrier gas passes through the sampling column, nothing happens on reversing the flow. If a solute comes out of the diffusion column at $z=0$ (cf. Fig. 2) as the result of its diffusion into the carrier gas, filling the column $z$ and also running along the...
Fig. 3. Part of a typical chromatogram obtained by RF-IGC for the system 1-C₄H₈/H₂/thin film ZnO, at 100 °C, concerning only adsorption.

Fig. 4. Part of a typical chromatogram obtained by RF-IGC for the system 1-C₄H₈/H₂/thin film Pd/ZnO, at 100 °C, concerning isomerization reaction.

Fig. 5. Part of a typical chromatogram obtained by RF-IGC for the system 1-C₄H₈/H₂/thin film Pd/ZnO, at 100 °C, concerning both isomerization and hydrogenation reactions.

A small quantity (1 cm³) of 1-butene gas was injected into the end of column L₂, and after the appearance of the continuously rising concentration–time curve, the reversing procedure for the hydrogen carrier gas flow started, each reversal lasting 3 s. This is shorter than the gas hold-up time in sections \( l \) and \( l' \) of the sampling column.

The narrow fairly symmetrical sample peaks created by the flow reversals were recorded and their height was printed as a function of time \( t \).

3. Calculations

The calculation of all physicochemical quantities has been based on the already published programs by Katsanos and Roubani-Kalantzopoulou [18–21]. The programs have been re-written in the Fortran language, including some modifications so that the standard deviations of the kinetic constants can be determined. These are available by the authors.

The main equation remains Eq. (1)

\[
H^{1/M} = gc(l', t) = \sum_{i=1}^{4} A_i \exp(B_i t)
\]

where \( H \) (cm) is the height of sample peaks resulting from the flow reversals, \( M \) (dimensionless) is the response factor of the detector, \( g \) (cm/mol cm⁻³) is the calibration factor of the detector, and \( c(l', t) \) (mol cm⁻³) is the measured sampling concentration of the injected gas at \( x = l' \).

The explicit calculation of the adsorption parameters for the hydrocarbon studied can be carried out in an analogous way to the one described earlier. All parameters refer to the values of \( c_y(0, t) \), i.e. the concentration of the gaseous analyte at \( y = 0 \):

\[
c_y(0, t) = \frac{vL_1}{D_z} c(l', t) = \frac{vL_1}{gD_z} \sum_{i=1}^{4} A_i \exp(B_i t)
\]

where \( v \) (cm s⁻¹) is the linear velocity of the carrier gas in the sampling column, \( L_1 \) (cm) is the length of the diffusion column and \( D_z \) (cm² s⁻¹) is the diffusion coefficient of the 1-butene into the hydrogen, which is used both as carrier gas and as the second reactant at the same time. From this, the value of the adsorbed concentration \( c_s^* \) is calculated

\[
c_s^* = \frac{\alpha_s}{\alpha_s k_1} \frac{vL_1}{gD_z} \sum_{i=1}^{4} \frac{A_i}{B_i} \exp(B_i t) - 1
\]

where the first fraction corresponds to the ratio of the cross-sectional area of the void diffusion column (cm²) to the amount of solid adsorbent per unit length of the same column (g cm⁻¹), \( k_1 \) (s⁻¹) is the local adsorption coefficient, and the rest of the symbols have been explained after Eq. (2). The local adsorption
Table 1
Kinetic constants for hydrogenation, \( k_2 \) and adsorption, \( k_R \) for the examined thin films in various temperatures

<table>
<thead>
<tr>
<th>( T (\degree C) )</th>
<th>( 10^4 k_2 (s^{-1}) )</th>
<th>( 10^3 k_R (s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/ZnO</td>
<td>Au/ZnO</td>
<td>ZnO</td>
</tr>
<tr>
<td>70</td>
<td>6.27 ± 0.39</td>
<td>–</td>
</tr>
<tr>
<td>80</td>
<td>–</td>
<td>2.46 ± 0.74</td>
</tr>
<tr>
<td>90</td>
<td>8.28 ± 3.18</td>
<td>2.85 ± 0.09</td>
</tr>
<tr>
<td>100</td>
<td>10.6 ± 0.30</td>
<td>2.29 ± 0.08</td>
</tr>
<tr>
<td>110</td>
<td>11.3 ± 0.40</td>
<td>2.79 ± 0.07</td>
</tr>
<tr>
<td>120</td>
<td>14.2 ± 0.20</td>
<td>3.12 ± 0.25</td>
</tr>
</tbody>
</table>

The isotherm is given by

\[
\theta_t = \frac{c_s^*}{c_{max}}
\]

where \( c_{max} \) is the local monolayer capacity, and \( c_s^* \) is given by Eq. (3).

\[
c_{max}^* = c_s^* + \frac{\partial c_s^*}{\partial c_y} KRT
\]

Thus, for the \( c_{max}^* \) determination the derivative \( \frac{\partial c_s^*}{\partial c_y} \) and \( KRT \) from Eqs. (6) and (7), respectively, are needed:

\[
\frac{\partial c_s^*}{\partial c_y} = \frac{\alpha_y}{\alpha_s} \sum_{i=1}^{4} A_i \exp(B_i t)
\]

\[
KRT = \frac{gD_z}{vL_1} \left[ \frac{\sum_{i=1}^{4} A_i B_i^2 \exp(B_i t)}{\sum_{i=1}^{4} A_i \exp(B_i t)} \right]^{1/2} - \frac{1}{\sum_{i=1}^{4} A_i \exp(B_i t)}
\]

In all equations above \( A_i \) and \( B_i \) are the pre-exponential factors and the exponential coefficients of Eq. (1). The relations for calculating the adsorption energy \( \varepsilon \) (kJ/mol) and the modified probability density function \( \varphi(\varepsilon; t) \) from experimental data are given by the following equations:

\[
\varepsilon = RT[\ln(KRT) - \ln(RT) - \ln K^0]
\]

\[
\varphi(\varepsilon; t) = \frac{\theta f(\varepsilon)}{c_{max}^*}
\]

where \( f(\varepsilon) = (\partial c_{max}^*/\partial \varepsilon) = (\partial c_{max}^*/\partial t)/(\partial \varepsilon/\partial t) \) is the density probability function for the adsorption energies.

Finally, the adsorption entropy \( \Delta S_{ads}^{\circ} \) is calculated from the following equations [25,26]:

\[
\Delta S_{ads}^{\circ}_{local} = -R \ln \left( \frac{\theta_t}{1 - \theta_t} \right) - S_{trans}^{g}
\]

\[
S_{trans}^{g} = R \ln(T^{5/2} MB^{3/2}) - 2.30
\]

\[
\frac{\partial(\Delta S)}{\partial t} = -R \frac{\partial}{\partial t} [\ln \theta_t - \ln (1 - \theta_t)] = - \frac{R}{\theta_t(1 - \theta_t)} (\partial \theta_t/\partial t)
\]

where \( \Delta S_{ads}^{\circ} \) (J/mol/K) local adsorption entropy, \( MB \) (kg/mol) molar mass of gas.

All the necessary relations for calculating the values of all the above adsorption parameters from Eq. (1), for the adsorption of gases on heterogeneous surfaces as a function of time, have been derived with the Jovanovic isotherm model:

\[
\theta(p, T, \varepsilon) = 1 - \exp(-K p)
\]
where

\[ K = K^0(T) \exp(\varepsilon / RT) \]  \hspace{1cm} (14)

\[ K^0 = \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}} \frac{\nu_g(T)}{b_g(T)} \]  \hspace{1cm} (15)

where \( m \) is the molecular mass of the adsorbate; \( k \) is the Boltzmann’s constant; \( h \) is the Planck’s constant; and the ratio \( \nu_s(T)/b_g(T) \) of two partition functions, namely that of the adsorbed molecule, \( \nu_s(T) \), and that for rotations–vibrations in the gas phase \( b_g(T) \). This ratio is taken as a unity as usual.

4. Results and discussion

It is the first time, where two different and popular methods namely PLD (for thin films development) and RF-IGC (for physicochemical characterization of films) are combined.

As regards the nano-particles presence, our previous results [5] showed that the cluster formation on the top follows the Volmer–Weber nucleation mode [27], that is, the small clusters, initially formed on the surface, grow then into larger islands. Indeed, atomic force microscopy (AFM) observations in [5] proved that the Au cluster distribution with an initially 30 nm average diameter flattens and shifts to larger diameters when increasing the deposition time up to 15 min. To be able to extrapolate the results of [5] to the present work about the cluster formation, we notice that we used here a different wavelength. We estimated therefore the absorption coefficients \( \alpha(\lambda) \) of Au for the two wavelengths 193 nm (this work) and 355 nm [5] and found that \( \alpha(193 \text{ nm}) \) is slightly (8%) larger than \( \alpha(355 \text{ nm}) \). The fact that we used half the laser fluence (3 J/cm\(^2\)) in this work speaks for a cluster formation of similar or even smaller Au nano-particles. As the Pd clusters are concerned, \( \alpha(193 \text{ nm}) \) is by a factor of 3 lower than that for Au and from the present deposition conditions (laser fluence and deposition time) and the results of Fig. 1 in [5], we estimate a cluster distribution with an average diameter around 40 nm.

The IGC technique with the corresponding time-resolved analysis is also used for the first time in order to characterize compounds in the nano-scale domain.
Hence the most important result is that the experimentally observed values of local isotherms and the other local adsorption quantities are influenced by the presence and the kind of nanoparticles as well as by the working temperature. From Figs. 3–5 one can conclude safely and accurately about chemical reactivity. Thus, it is obvious that hydrogenation takes place in the case of Pd/ZnO thin films [28]. This fact is demonstrated by the chromatograms obtained, where one or two new peaks, which belong to the product(s) of this heterogeneous catalysis, appear.

Depending on the experimental conditions, the catalytic reaction may stop at the isomerization or proceed to hydrogenation. In any case, both isomerization and hydrogenation are catalytic reactions were the catalyst is the thin film Pd/ZnO. A third case [28] corresponds to the direct appearance of butane (in the presence of pure Pd) by overcoming the isomerization reaction.

More precisely, in Fig. 5, where three distinct peaks appear, isomerization of the double bond of 1-butene takes place before its hydrogenation. The first peak corresponds to butane, the second one to 1-butene and the third to the isomerized by-product [28].

By the time resolved analysis, it is also obvious that the appearance of a product-peak is clearly a function of temperature. That is, the time of appearance of this new peak is higher at 70 °C and lower at 140 °C.

The height $H$ of the sample peaks, when plotted versus time $t$, gives the so-called diffusion band. At first, a significant observation had taken place. We have checked the behaviour of the bulk material (in powder form) regarding that of the monolayer (in thin film form) and we have found exactly the same behaviour. The diffusion bands, which result experimentally, are identical. An important difference in the behaviour of the diffusion bands is observed (cf. Fig. 6) concerning the thin films of ZnO, Au/ZnO and Pd/ZnO. As regards the ZnO and Au/ZnO films, the temperature does not influence the diffusion bands at all, as the slope is the same. On the contrary, the Pd/ZnO thin film differs significantly, as the temperature influences the slope of the diffusion band strongly. More specifically, the slope of the descending part of the curve becomes more abrupt as the temperature increases. It is concluded that the rate of reactant consumption increases with the increase of temperature. From the time of 70 min and on, the slope of all diffusion bands becomes identical at all temperatures, except for the temperature of 70 °C. Taking into consideration the different slopes of the diffusion bands, the
determination of kinetic quantities is achieved, according to Van 't Hoff method (method of initial rates).

From the comparison of the values (cf. Table 1) concerning the rate coefficient of the surface reaction, $k_2$ and the adsorption coefficient, $k_R$ ($k_{\text{adsorp.}}/k_{\text{desorp.}}$) an increase of $k_2$ and $k_R$ is realised for the thin film Pd/ZnO with the parallel increase of temperature. This fact implies that the active sites, which Pd creates, strengthen the process of catalytic reaction to a large extent as regards the net ZnO film [29–31]. On the contrary, the deposition of Au nano-particles on the ZnO does not help in the particular catalysis, which is also argued bibliographically since the hydrogen is not adsorbed by the Au. As a result, Au nano-particles decrease the free sites, likely for reaction, on the ZnO surface, something that was expected. It is important to report that Au had been chosen to be used, as the main interest of this work was not only the catalytic and the adsorption efficiency of thin films with or without different kinds of nano-particles deposited on them but also to check the catalytic reactions.

In Figs. 7–13, the local adsorption quantities concerning ZnO, Au/ZnO, and Pd/ZnO thin films are presented.

From the diagrams $\theta_t - t$, $\varepsilon - t$, $\varphi(\varepsilon; t) - t$, $c_{\text{max}} - t$ (cf. e.g. Fig. 7), a great difference of the system Pd/ZnO against the other two is obvious. This is due to the powerful effect of Pd nano-particles on the catalytic surface reaction.

The local adsorption isotherm refers to the surface coverage of thin film in respect to time. In other words it shows the percentage of the covered active surface sites in the corresponding time. A standard behaviour, independent of temperature, is observed concerning thin films ZnO and Au/ZnO (cf. Fig. 7). On the contrary, for the thin film Pd/ZnO an important change of
Fig. 12. Local monolayer capacity for thin film (a) ZnO, (b) Au/ZnO and (c) Pd/ZnO.

local adsorption isotherm, $\theta_t$, is noticed. In particular, the value of the second maximum increases as the temperature increases with a parallel decrease of the corresponding time. This means that in the case of Pd nano-particles the adsorption of gases from the catalytic rod is influenced not only by the kind and the structure of the thin film but also by the temperature. Especially, at high temperatures (100, 120 $^\circ$C) the phenomena taking place are completed faster.

As regards the local adsorption energy, $\varepsilon$, the experimental results are plotted in Fig. 8. The term “local” means the mean value of $\varepsilon$ for the adsorption sites $i$ being responsible for the adsorption at time $t$. The adsorption energy change with respect to time shows three different regions. Initially, it is maximised and then minimised (at the same time with that of the corresponding adsorption isotherm). Is this due to the creation and destruction of new adsorption sites with time? The answer is yes, as different collections of adsorption sites are involved at different times. The first one corresponds to the local sites active at the beginning of the experimental time. In the second part some other energies appear lower than the first ones. These correspond to the new active sites, which are owed to the lateral interactions. The third one corresponds to higher experimental time values. The obvious conclusion is that, owing to the dynamic procedure, transition adsorption energies are observed experimentally leading to the final levelling off of their values. As regards the influence of the temperature, a small shift to higher values is recorded at higher temperatures for all three thin films. Of course, the values of $\varepsilon$ are much higher in the case of Pd/ZnO than those for ZnO and Au/ZnO, at the same temperature. This means that the adsorption of the reactants is easier in the first mentioned thin film.

When the probability density function, $\varphi(\varepsilon; t)$, is plotted against the experimental time (cf. Fig. 9) the different regions of active centres are very well separated in time and their relative population can easily be calculated by simply finding the corresponding areas under the time curve of the different separate peaks [32]. Again this plot gives three distinguished parts corresponding to three different kinds of active sites produced at different times. Thus, for small time spans the sites of higher energy, which correspond to the minima of adsorption potential, are filled first, then, because of the lateral interactions, the sites corresponding to the second curve appear. Finally, the third kind of adsorption with smaller energy may be attributed to molecules very loosely bound to the substrate. Especially, regarding the Pd/ZnO film, differences are observed at the various temperatures. A descending part is noticed initially and then two peaks
(three peaks at 120 °C) are presented which appear at smaller times as the temperature increases. From this behaviour it can be concluded that the adsorptive regions are activated earlier at higher temperatures. On the contrary, in the cases of ZnO and Au/ZnO thin films the probability density function remains roughly the same at all the temperatures.

As far as the concentration of non-adsorbed 1-butene \( c_v \), corresponding to thin films ZnO and Au/ZnO is concerned (cf. Fig. 10), identical behaviour is observed, independent of temperature. That means that 1-butene does not react to give product. On the contrary, for the Pd/ZnO thin film an abrupt change of the slope is noticed with the increase of temperature, which shows the great dependence of catalytic reaction from the temperature. Thus, this fact strengthens the ascertainment that the deposition of Pd favours the process of hydrogenation, since a significant reduction of 1-butene concentration is observed up to 70 min. From the time of 70 min and on, the slope of all curves becomes identical at all temperatures, except for the temperature of 70 °C.

The same observation is valid for the diffusion bands (which are mentioned above). The appearance of the functions \( c_v = f(t) \) is identical to the so-called diffusion bands of the RF-IGC method (i.e. it has a small increase initially, passes through a maximum and then declines with time, cf. Fig. 11). From Fig. 11 it is shown that the plot of local non-adsorbed 1-butene concentration versus time and the corresponding diffusion band are identical for each system. It is admirable how a theoretically determined quantity (the local non-adsorbed reactant concentration), which comes out from the mathematical model, coincides with the diffusion band, a clearly experimental finding (height of the chromatographic peaks against time). This fact shows that the results from the experiment and the mathematical model are always in total agreement.

As results from Fig. 12, thin films of Au/ZnO display smaller values of local monolayer capacity \( c_{s \text{max}}^{e} \) than ZnO films at the same temperature (referring to the part from the maximum until the completion of the experiment). This can be explained by the fact that certain active sites of the film surface have been covered by gold nano-particles that do not allow the adsorption of 1-butene. That is to say that the deposition of nano-particles Au on the solid surface ZnO does not favour this kind of catalysis. In the case of thin film Pd/ZnO, smaller values of \( c_{s \text{max}}^{e} \) are obtained, even though the hydrogenation is encouraged due to Pd nanoparticles and higher values would be expected. However, in this case, the continuously formed product occupies certain places of surface. Thus, the free sites are decreased and therefore the adsorbed reactant quantity is less.

There are two publications regarding entropy values determination with RF-IGC method [25,33], but results of adsorption entropy versus time concerning thin films (cf. Fig. 13) are presented for the first time. The change of the slope is due to the phenomena taking place on the surface of thin films. The descending part of the curve corresponds to adsorption. During this, decrease of entropy takes place, which is justified by the fact, that some degrees of freedom owing to the transitional and rotational movements of 1-butene molecules are lost. The ascendant part corresponds to desorption and surface catalytic reaction, that causes increase of the value of adsorption entropy as a consequence of the increase of disorder, up to a finally re-establishment of equilibrium.

The superiority of RF-IGC becomes obvious as this method can account for mass transfer and desorption phenomena under non-steady state conditions. By using this technique, it is also possible for one to study the mechanism in detail, because of the possibility of kinetic constants determination concerning all the stages (cf. Table 1). Thus, the adsorption/desorption phenomena are studied in the presence of the main surface reaction. All these lead to the conclusion that the RF-IGC method can offer a lot to catalytic studies.

It is also obvious that the above method is capable of achieving the classification of the thin films Pd/ZnO, ZnO and Au/ZnO regarding their catalytic activity. At the same time the physicochemical characterization of the surface of thin film catalysts is also achieved. Consequently, it must also be stressed that the success of RF-IGC to investigate the catalytic behaviour of thin films where the later are in nano-scale dimensions is obvious. It is important to report that adsorption entropy values are calculated, a fact which constitutes an innovation of the RF-IGC.

5. Conclusions

The object of this work was the study of fundamentals of adsorption and heterogeneous catalysis in thin film structures, a benefit for the understanding of catalytic properties of thin films in the form of metal/metal oxide, prepared by PLD. Moreover, the RF-IGC proved to be a powerful tool for studying the topography of active sites of heterogeneous surfaces in the nano-scale domain. Thus, some very important quantities for the surface chemistry have been determined for all three thin films studied. These physicochemical local quantities have been determined from the experimental \( H, t \) pairs by a nonlinear least-squares method, through personal computer programs written in Fortran, which are available by the authors upon request. Through the time-resolved analysis a surface characterization of the examined thin films took place without using retention volume data. In addition, the kinetic constants responsible for adsorption, desorption and surface chemical reactions have also been calculated.

References