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Surface studies by reversed-flow inverse gas chromatography: A review

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Last and not least, this work is dedicated in the memory of my mother Dionysia.

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ABSTRACT

In the present work, the application of reversed-flow inverse gas chromatography (RF-IGC) to adsorption studies related to heterogeneous catalytic processes on noble metal supported catalysts is reviewed. RF-IGC methodologies are technically simple and they are combined with suitable mathematical treatments which give the possibility for studying the kinetics of catalyzed surface reactions, as well as the topography and the nature of the active sites of solid catalysts. Adsorption parameters, such as rate constants, adsorption energies, adsorption entropies, local isotherms, surface diffusion coefficients, lateral interaction energies and energy distribution functions, are simultaneously determined by RF-IGC. The potential of the novel methodologies has been evaluated by utilising as model systems CO adsorption/oxidation over well-studied Pt–Rh/SiO_2 and nanosized-Au/γ-Al_2O_3 catalysts. The main findings are presented and future goals are also discussed.

1. Introduction

During the last decades, the development of catalysts has been related to many aspects of technological and environmental interest. Heterogeneous catalysis contributes to the creation of a very large fraction of global economic wealth. Heterogeneously catalyzed reactions are at the center of energy production, pollution remediation, as well as the production of chemicals and pharmaceuticals [1,2].

Around World War I, Langmuir proposed a simple theory of chemisorption and showed how it could be used to formulate rate laws for reactions occurring on surfaces. From that time on, surface science has been playing an important role in heterogeneous catalysis. Between the two world wars, simple quantitative studies of adsorption by catalyst surfaces led to the concept of activated adsorption and to a universally used method for determining the high surface areas associated with the pore structures of catalytic materials. After World War II, the application of various spectroscopic and structural probes made possible the investigation of catalyst surfaces at a more microscopic level. Studies with idealized surfaces such as the faces of single crystals in ultra-high vacuum apparatus also made their appearance. By the end of the twentieth century, direct information was being obtained on the rates of elementary reactions of well-defined surface species [3]. Over the past 40 years, surface science has evolved to become both an atomic scale and a molecular scale science. Various concepts, instruments, and model systems that enabled the rapid evolution of surface science, have been developed permitting the better understanding of the various catalytic processes which can significantly assist the preparation of more active and selective catalysts [4].

On the other hand, gas chromatography is presumably known as a separation method which is based on elementary processes such as: diffusion, adsorption/desorption and chemical equilibrium of the studied solutes between the mobile and the stationary phase. However, these physicochemical processes are also steps of the heterogeneously catalyzed reactions and consequently suitable combinations of instrumentation and mathematical analysis of the chromatographic data can give information about the above mentioned processes. The chromatographic methods, which are used for physicochemical studies, usually lead to precise and accurate results with relatively cheap instrumentation and a very simple experimental setup [5,6].

Some of the physicochemical properties measured by GC pertain to solutes dissolved in the mobile carrier-gas phase, but the majority of these properties refer to the stationary phase (e.g. catalytic properties of a solid stationary phase). This is known as inverse gas chromatography (IGC) and has the stationary phase of the system as the main object of investigation. In IGC the same procedures as in direct GC are employed, but the quantities measured are used to derive properties of the stationary phase. Based on the broadening factors embraced by the Van Deemter equation, gas chromatography and particularly inverse gas chromatography (IGC) have been applied in measurements related to physicochemical phenomena [7].

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Reversed-flow inverse gas chromatography (RF-IGC) is a novel IGC method. In this technique, instead of basing physicochemical measurements on retention volumes of elution peaks, their broadening and their shape distortion, due to physicochemical processes is under study. RF-IGC is based on reversals of the direction of the carrier-gas flow at various time intervals. In this way, a repeated sampling of slow rate processes taking place within the chromatographic column can be carried out. Using suitable mathematical analysis of the experimentally obtained chromatographic data a big amount of physicochemical parameters have been estimated among of the others: adsorption equilibrium constants, gas diffusion coefficients in binary and ternary mixtures, activity coefficients, mass transfer coefficients on solids and liquids, solubility and interaction parameters in polymer-solvent systems, molecular diameters and critical volumes in gases, Lennard–Jones parameters, as well as rate constants and activation parameters [8–15].

Nieuwenhuys is recognized as one of the pioneers in the area of catalytic surface science in Europe. He has built up the surface science laboratory at the Leiden Institute of Chemistry and he has created a wide network of collaborations all over the world. His work is highly respected among of the others in catalysis by gold and Pt–Rh alloys [16–21]. During the last decade, in the framework of our collaboration with Prof. Nieuwenhuys, reversed-flow gas chromatography has been further extended in studying the kinetics as well as the heterogeneity and the nature of the active sites of noble metal supported catalysts. The potential of these novel methodologies has been evaluated by using well-studied bimetallic Pt–Rh/SiO_2 and Au/γ-Al_2O_3 catalysts. In the present work the main findings of the application of RF-IGC to surface studies related to heterogeneous catalytic processes on noble metal supported catalysts are presented and discussed.

2. Material and methods

2.1. General

Conventional GC involves the flow of a gaseous mobile phase in a defined direction over a stationary phase or packing resulting in the selective retention of solute components. In RF-IGC the system is modified; and another column (diffusion column) is placed perpendicularly in the center of the conventional chromatographic column (sampling column). The carrier-gas flows continuously through the sampling column, while it is stagnant into the diffusion column, at which open end the studied catalyst bed is usually placed, as shown in Fig. 1. The displacement of the injected solute (e.g. CO, O_2 or CO_2) into the diffusion column depends on its interaction with the stationary phase (e.g. adsorption, desorption and surface bonding) as well as its diffusion into the stagnant carrier-gas (mobile phase), while it is independent of the carrier-gas flow-rate making RF-GC an ideal method for studying slow rate processes.

Another feature of the technique is the sampling procedure of the physicochemical phenomena, taking place into the diffusion column. Carrier-gas flow reversals are done for a short time by using a four-port valve and then the flow is restored in its original direction. The above-mentioned flow reversals procedure results in a short enrichment of the solute quantity into the carrier-gas and extra chromatographic peaks are created on the continuous concentration–time curve (chromatogram). The extra peaks are symmetrical and their height or area is proportional to the concentration of the solute in the junction of the diffusion and sampling columns [8].

Summarizing, utilizing RF-IGC methodologies it is possible to carry out surface studies either under steady (placing the catalyst bed at a short length of the sampling column near the junction of the diffusion and sampling column) or non-steady-state conditions (locating the catalyst bed at a short length at the entrance of the diffusion column L). The advantages of RF-IGC methodologies have been presented in detail elsewhere [8–15].

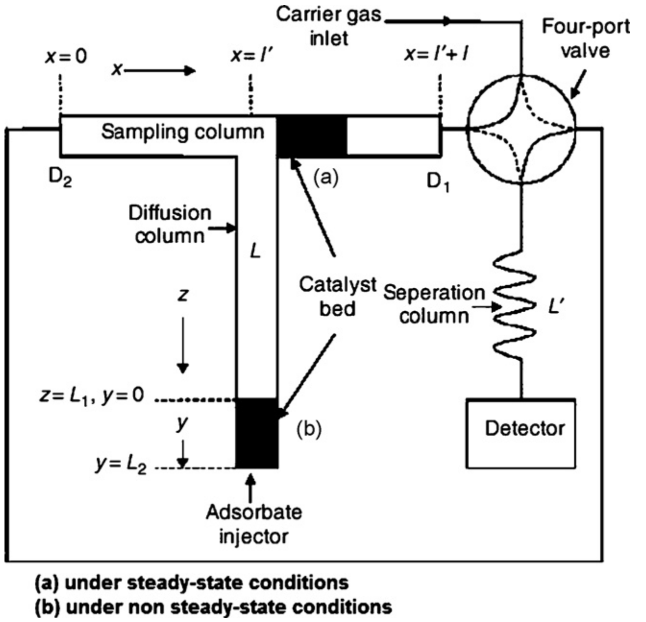


Fig. 1. Experimental setup used from RF-IGC for the characterization of solid catalysts: (a) under steady-state conditions and (b) under non-steady-state conditions.

2.2. Materials

The studied noble metal catalysts were: (1) Pure Pt and Rh supported on SiO_2 (3%, w/w), as well as 75% Pt + 25% Rh, 50% Pt + 50% Rh and 25% Pt + 75% Rh alloys supported on SiO_2 (3%, w/w). The method of preparation and the surface characterization of the catalysts using TDS and XPS have been presented previously [16,17]. (2) Nanometer sized Au/γ-Al_2O_3 catalysts with an intended 5 wt.% composition were prepared by homogeneous deposition precipitation with urea. All gold catalysts were filtered, washed to remove Cl^- and dried in air at 80 °C for at least 16h and then calcined in a flow of oxygen up to 300 °C (heating rate 5 °C min^{-1}). The samples were kept at 300 °C for 2 h, and then cooled to room temperature. The method of preparation and the surface characterization of the catalyst using AAS, XRD, HRTEM, XPS and MES, have been presented previously (18–20). The gold loading determined by AAS was 5.1 ± 0.3%, while the mean diameter of the gold particles was measured 4.2 nm (XRD) and 3.6 ± 1.4 nm (HRTEM), respectively. Before use all the studied catalysts were reduced at 628 K for 10 h in flowing hydrogen at a flow-rate of 1.0 $cm^3 s^{-1}$.

The separation column, L', for the separation of CO and its possible dissociation product CO_2, was filled with filled silica gel (80–100 mesh) from Supelco, (Bellfonte, PA, USA). Hydrogen, from Linde (Patras, Greece) (99.999% pure) was used for the reduction of the catalysts, while carbon monoxide, carbon dioxide and oxygen from B.O.C. Gases (Athens, Greece) (99.997% pure), were used as adsorbates.

Helium, from BOC Gases (Athens, Greece) (99.999% pure) was used as carrier-gas in CO, O_2 and CO_2 sorption experiments. For studies simulating CO oxidation a helium/oxygen mixture prepared by B.O.C. Gases (Athens, Greece), consisting of 93% He + 7% O_2 (v/v, 99.999% pure) was the carrier-gas. In experiments in which the effect of H_2 in CO adsorption was studied, different composition hydrogen/helium mixtures prepared by B.O.C. Gases (Athens, Greece) were used as carrier gases. Their compositions were: 25.05% H_2 + 74.95% He (v/v, 99.999% pure), 49.95% H_2 + 50.05% He (v/v, 99.999% pure) and 75.05% H_2 + 24.95% He (v/v, 99.999% pure), respectively.

2.3. Methods

The experimental setup of RF-IGC and the procedure for the study of catalytic processes has been presented elsewhere [15,22,23].

3. Theory and calculations

Since the area or the height H, of the sampling peaks is proportional to the concentration of the substance under study, at the junction, $x = l'$, of the sampling cell, at time, t, from the beginning of the experiment [8], if $\ln H$ is plotted against time t for each solute, the so-called "*diffusion band*", is obtained. An example is shown in Fig. 3 of Ref. [22].

3.1. Under steady state conditions

Having placed the catalyst bed at a short length of the sampling column near the junction of the diffusion and sampling column (c.f. Fig. 1), the catalytic behaviour under steady-state conditions can be studied. In that case, time dependent fractional conversions X_t are determined from the heights or the areas of the sampling peaks obtained after each flow reversal and, overall conversions X can be calculated from the total areas of the "*diffusion bands*" corresponding to reactants and products.

3.2. Under non-steady state conditions

Having placed the catalyst bed at a short length at the entrance of the diffusion column L, as shown in Fig. 1, the catalytic behaviour under non-steady-state conditions can be studied. In that case not only conversions but a large number of physicochemical parameters related to the interaction of the studied catalyst with the injected adsorbate are determined. The whole treatment of experimental data is based on the fact that the heights of the "*sampling peaks*" are described by a clear function of time comprising the sum of 2–4 exponentials.

$$H^{1/M} = \sum_i A_i \ \exp(B_i t) \qquad (1)$$

where: H are the heights of the experimentally obtained chromatographic peaks, M the response factor of the detector and t the time from the beginning of the experiment. The values of the pre-exponential factors A_i and the corresponding coefficients of time B_i are easily and accurately determined from the chromatogram by PC programmes of nonlinear least-squares regression (c.f. Appendix of Ref. [14]).

The "*sampling peaks*" resulting from the flow reversals are recorded and their heights or areas are measured together with the corresponding time t. These experimental pairs of values H, t are the variables of Eq. (1). By introducing them into the data lines of the GWBASIC program given in the Supporting Information of Ref. [14], together with other quantities required by the input lines, various adsorption parameters are calculated. A short presentation of the calculations is summarized in Fig. 2. The estimated physicochemical quantities are saved in data archives. Importing these data in usual PC software (Excel, Origin, etc.) curves of pairs of the above mentioned quantities are constructed.

4. Results and discussion

4.1. Activity and kinetic studies over Pt–Rh/SiO$_2$ alloy catalysts

The oxidation of carbon monoxide on noble metals is one of those reactions that have used to define the field of heterogeneous

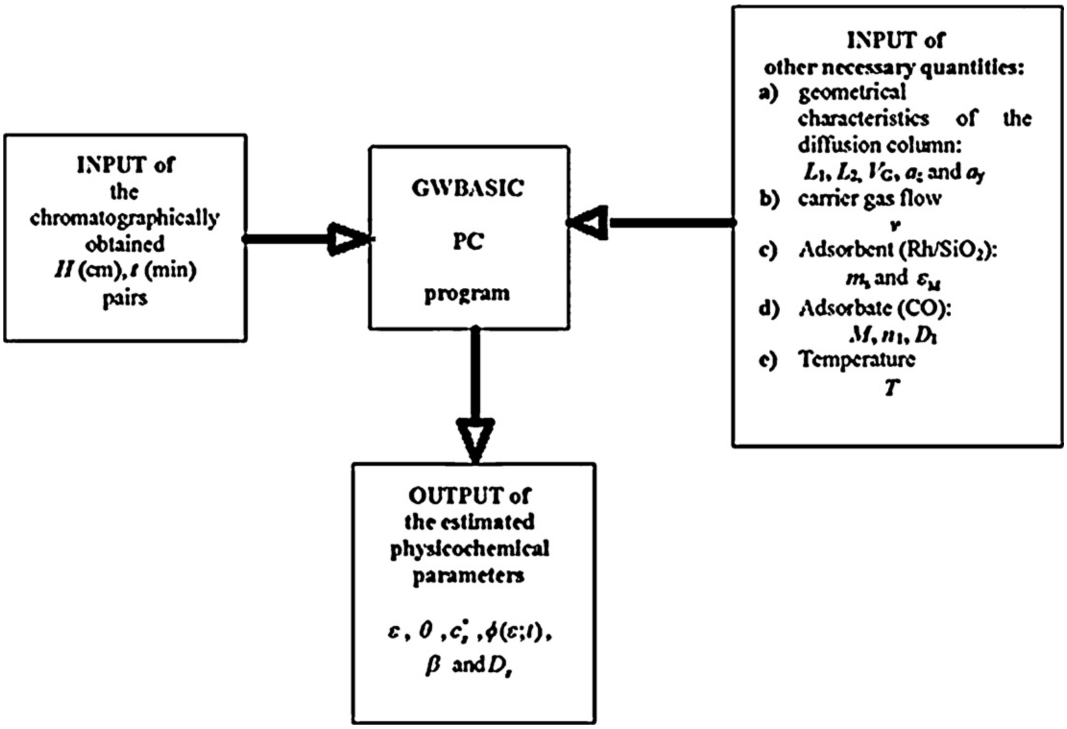


Fig. 2. Schematic representation of the experimental determination of physicochemical surface quantities, for CO adsorption over Rh/SiO$_2$, by RF-IGC. The chromatographically obtained data are the sampling peaks heights, H, and the respective time, t, which are imported in appropriate GWBASIC PC-programs. Other necessary quantities also imported are: the geometric properties of the diffusion column: L_1, L_2, a_y, a_z and V_G, the corrected linear flow velocity of the carrier-gas, v, adsorbent's mass, m_s, and porosity, ε_M, adsorbate's molecular weight, M_1 and amount, n_1 (moL), as well as the diffusion coefficient of the injected adsorbate into the carrier-gas, D_1.

catalysis. It was one of the reactions used by Berzelius to invent the word "catalysis". Its kinetics and mechanism have been extensively studied since this reaction has significant technological importance for the remediation of air pollution. In the majority of the heterogeneous catalysts, the active phase (usually noble metals or metal oxides) are supported over a porous solid material such as silica, alumina, etc. Most of the catalysts used for the control of automotive emissions contain platinum or palladium to catalyze the oxidation of carbon monoxide and hydrocarbons, as well as rhodium to promote the reduction of nitric oxides. Supported bimetallic catalysts exhibit certain desirable properties (e.g. improved activity and selectivity, thermal stability, poison resistance, etc.) which are absent in the individual metals.

Well-studied silica-supported three-way catalysts [16,17], containing both platinum and rhodium were studied by RF-IGC methodologies and physicochemical parameters related to the activity and the kinetics of the elementary steps of CO oxidation (adsorption, desorption, surface reaction) have been determined. These parameters were: (1) time depended, X_t, and overall, X, conversions, either under steady or non-steady-state conditions [23–26] and adsorption, k_1, desorption, k_{-1}, and surface reaction, k_2, rate constants and the respective activation energies, E_a [25–28].

Catalytic fractional conversions of CO to CO_2 over Pt–Rh alloy catalysts, in the presence of excess oxygen, under steady-state or non-steady-state conditions, as well as the corresponding rate constants for CO oxidation reaction were determined. From the temperature variation of the conversions, their maximum values were found, which depend on the catalyst nature (Pt content). Those results suggested a synergism between Pt and Rh in the Pt–Rh bimetallic catalysts in accordance with previous works [24].

CO dissociative adsorption over silica-supported Pt, Rh and Pt–Rh alloy catalysts was observed in sorption experiments (using pure He as carrier-gas) and was further kinetically studied [25]. It was found that the most active catalysts concerning CO dissociation were the bimetallic ones. At temperatures lower than 400 °C, $Pt_{0.50}$ + $Rh_{0.50}$ and pure Pt catalysts activity was similar while at higher temperatures the dissociative activity of Rh catalyst became more intense. Moreover, for all the studied catalysts the values of the adsorption and desorption rate constants, k_1 and k_{-1}, increased with rising temperature indicating that the relevant processes are activated. In contrast, the rate constants, corresponding to the dissociation reaction, k_2, over the bimetallic, $Pt_{0.50}$–$Rh_{0.50}$ catalyst, exhibit a behaviour similar to that of the conversion of CO to CO_2, increasing to a maximum value, at 370 °C and then, decreasing. The values of the estimated activation energies were significantly lower, compared to those mentioned in literature indicating corrugated surfaces. From the differences in the found energy barriers, it was concluded that CO adsorption is more activated than CO disproportionation reaction suggesting that CO adsorption may be the rate-determining step, followed by the dissociation step.

Information for the elementary steps of CO oxidation was obtained by studying CO, O_2, and CO_2 sorption on Pt–Rh bimetallic catalysts, in the absence of oxygen from the carrier-gas. The sorption of an adsorbate over an adsorbent includes steps such as adsorption/desorption and possible surface bonding or reaction. All the rate constants for CO adsorption (k_1), desorption (k_{-1}), and disproportionation reaction (k_2) were found to increase with rising temperature. In contrast the rate constants for oxygen adsorption, k_1, on the Pt-rich alloy catalyst ($Pt_{0.75}$–$Rh_{0.25}$) and for CO disproportionation reaction, k_2, over the Rh-rich alloy catalyst ($Pt_{0.25}$–$Rh_{0.75}$), decreased with rising temperature in agreement with the findings of other groups. The anomalous behaviour of oxygen adsorption rates was explained in the basis that Pt surface concentration in the Pt-rich catalyst compared to the Rh surface concentration, according to the surface phonon softening model, becomes larger with rising temperature. Considering that Pt surface in the Pt–Rh alloy catalysts is predominantly covered with CO, while Rh strongly adsorbs oxygen, the adsorption of oxygen on the Pt-rich catalyst can decrease at higher temperatures. On the other hand, the behaviour of the experimentally determined CO dissociation rates was explained by the fact that this catalyst is the most active for CO dissociation reaction, in agreement with the present rates and literature data [26]. The dependence of activation energies for adsorption, desorption and disproportionation reaction against the catalysts Pt content indicated that the activity of CO oxidation was more intense on the Pt-rich catalyst, while for CO dissociation reaction the most active was the Rh-rich catalyst [27].

Following the activity studies and the investigation of the kinetics of the elementary steps of the reactants and products of CO oxidation, the kinetics of CO oxidation in the presence of excess oxygen over Pt–Rh alloy catalysts were studied. A novel mathematical analysis developed and rate constants as well as the respective activation energies, for the oxidation of CO, as well as for its adsorption and desorption on and from pure Pt, $Pt_{0.75}$–$Rh_{0.25}$, $Pt_{0.50}$–$Rh_{0.50}$, $Pt_{0.25}$–$Rh_{0.75}$ and pure Rh silica-supported catalysts, were determined [28]. These results also ascertained the synergism between Pt and Rh.

4.2. *Kinetic studies of the effect of hydrogen on CO adsorption over Pt–Rh/SiO_2 alloy and Au/γ-Al_2O_3 catalysts*

Spurred on by the promise of significantly higher efficiency and almost no emission of pollutants, proton exchange membrane (PEM) fuel cells have been extensively studied in the last two decades for many applications especially for automobile propulsion and auxiliary power units. Hydrogen can be produced on-board by means of steam reforming of gasoline, methanol or other fuels. The resulting gas mixture typically ~75% H_2 and ~25% CO_2 is, however, contaminated with ~1% of CO which severely degrades the fuel cell performance by poisoning of the Pt (or Pt–Ru) anode. Hence, an efficient catalyst must be highly active in CO oxidation at temperatures compatible with the operation of the PEM fuel cell (70–100 °C) and very selective towards CO_2 formation. In contrast to well-studied CO oxidation, selective oxidation of CO in hydrogen-rich stream and moreover, CO adsorption in a H_2-rich atmosphere, which is a fundamental step for its selective oxidation are subjects that remain not well studied.

For these reasons a preliminary study of CO adsorption over Rh/SiO_2 catalyst, at 100.0 °C was carried out [29]. This particular catalyst was selected because it expected to combine high selectivity and satisfactory activity, in conditions compatible with the operation of hydrogen-PEM fuel cells. In order to examine the effect of hydrogen, three different composition hydrogen/helium mixtures, containing 25, 50 and 75% of H_2, were used as carrier gases. The most important finding of this work was that CO adsorption becomes higher as hydrogen carrier-gas amount increased. This was concluded both by the chromatographic and the kinetic findings.

Then the effect of hydrogen on CO sorption was further kinetically studied in a wide temperature range (60–250 °C), over both monometallic Rh/SiO_2 and bimetallic $Rh_{0.50}$ + $Pt_{0.50}$/SiO_2 catalysts [30]. Three different composition hydrogen/helium mixtures, ranging from 25 to 75% of H_2, were used as carrier gases, simulating H_2-dilute and H_2-rich conditions. The kinetic findings revealed that at low temperatures and under H_2-rich conditions, compatible with the operation of PEM fuel cells, the activity of the monometallic and the alloy catalysts was similar, but the selectivity of $Rh_{0.50}$ + $Pt_{0.50}$ alloy catalyst was higher, making Pt–Rh alloy catalyst as a better candidate for CO preferential oxidation, as expected from the comparative plots of Fig. 3. The found low energy barrier values were attributed to high surface amounts of CO. The desorption barriers were in any case much lower than the respective activation energies found for CO desorption in the absence of hydrogen indicating a H_2-induced desorption, which explained the observed in the literature rate enhancement of selective CO oxidation.

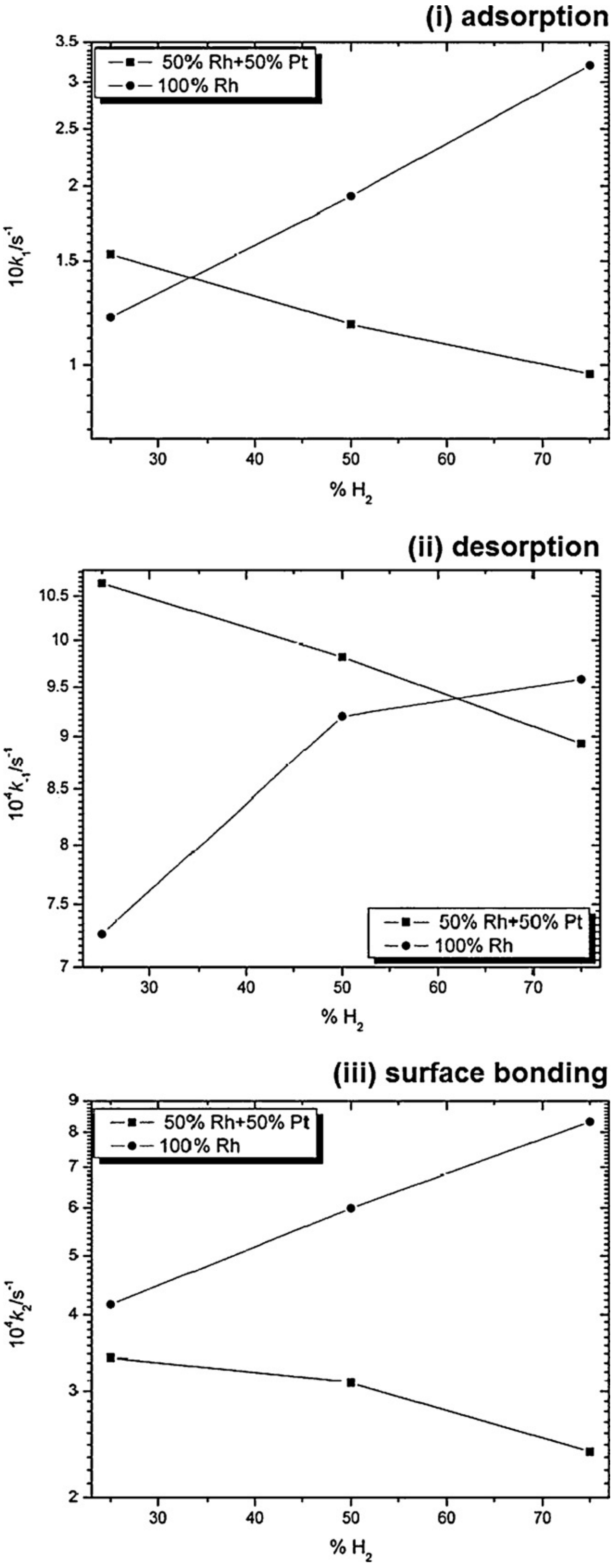


Fig. 3. Comparative presentation of the variation of the rate constants for CO (i) adsorption, k_1, (ii) desorption, k_{-1}, and (iii) surface binding, k_2, over silica-supported monometallic Rh and bimetallic Pt–Rh catalysts, against the percentage of H_2 in carrier-gas feeding stream, in a semi-logarithmic scale.

Nanometer-sized gold particles on oxide supports are efficient catalysts for the selective catalytic oxidation (SCO) of CO under conditions compatible with the operation of PEM fuel cells [18–20]. CO (reactant) and CO_2 (product) sorption processes are fundamental elementary steps for SCO and moreover, the effect of hydrogen on their sorption over supported Au catalysts remains a subject of significant interest. In a recent work, new findings gave further information on the mechanism of carbon monoxide selective oxidation over γ-Al_2O_3 supported nanosized Au catalysts [31]. For first time, it was observed, from activity studies that the adsorption of CO, over Au/γ-Al_2O_3 catalyst in the absence of oxygen, results in CO_2 formation, pointing to a model of active sites consisting of an ensemble of metallic Au atoms and a cationic Au with a hydroxyl group. A corresponding reaction mechanism was suggested, involving the insertion of CO into Au^+–OH^- to form Au-hydroxycarbonyl, which is then oxidized to a bicarbonyl, most probably interacting with O from neighboring Al-hydroxyl. Another new observation was CO_2 reversed water gas shift reaction, resulting in H_2 and CO_2 consumption towards CO and H_2O formation, which also contributes to the drastic decrease of SCO activity and selectivity, at high temperatures ($T > 200\,^\circ C$).

The kinetic study, carried out by RF-IGC revealed that at lower temperatures ($T < 150\,^\circ C$), the rate of CO adsorption, k_1, over Au/γ-Al_2O_3 was higher in excess of hydrogen compared to that in its absence from the carrier-gas stream, which is consistent with the observation that reduced in hydrogen samples have higher CO adsorption capacity. The rate of CO desorption, k_{-1}, was higher in excess of hydrogen, indicating a beneficial influence of hydrogen on CO desorption. In contrast, the rate constants corresponding to CO surface bonding, k_2, over the studied Au/γ-Al_2O_3 catalyst in the absence of hydrogen, k_2, were higher than those corresponding to the surface bonding of CO on the catalysts active sites, in excess of hydrogen, indicating the weaker and more reversible adsorption of CO.

A following work was focused on the kinetic investigation of the effects of H_2 and CO_2 on the rates related to the elementary steps of CO sorption over Au/γ-Al_2O_3 [32]. The kinetic study was carried out in a wide temperature range (50–300 °C). The findings of preliminary coadsorption studies of CO with H_2, O_2 and $O_2 + H_2$ indicated that a reductive pre-treatment of the Au catalyst with a mixture of CO in excess of H_2 can be more beneficial concerning CO oxidation activity at low temperatures, compared to the usual reduction in a diluted hydrogen atmosphere, most probably due to the easier activation of oxygen molecules. At high temperatures the rate of reversed water gas shift reaction became significant resulting in H_2 and CO_2 consumption. The kinetic findings indicated that the strength of CO_2 bonding was higher compared to that of CO and it further increased at higher temperatures in agreement with the observed deactivation of the selective CO oxidation in the presence of CO_2.

4.3. *Surface studies on Pt–Rh/SiO$_2$ alloy and Au/γ-Al$_2$O$_3$ catalysts*

The nature of the active sites is one of the pervasive problems in heterogeneous catalysis and in chromatography. In the case of a real solid the information on the heterogeneity of the surface is given by a distribution of the site energies.

$$\Theta(p,T) = \int_0^\infty \theta(\varepsilon,p,T) f(\varepsilon)\, d\varepsilon \tag{2}$$

Any two of the functions Θ (experimental adsorption isotherm), θ (unknown local isotherm) and $f(\varepsilon)$ (unknown distribution function of the adsorption energy ε) are needed to calculate the remaining one [34]. Inverse gas chromatography has been utilized for the estimation of surface heterogeneity studies [33–36].

Recently, a novel methodology of RF-IGC has been developed to study the surface topography and the nature of the active sites of heterogeneous surfaces [37]. The physicochemical parameters determined by RF-IGC, related with the investigation of the surface heterogeneity are (adsorption, desorption and surface reaction) rate constants, local adsorption energies, ε, local isotherms, $\theta(p,T,\varepsilon)$, local equilibrium concentrations on the surface, c_s^*, surface diffusion coefficients, D_s, lateral interaction energies, β, and adsorption energy distribution functions, $\varphi(\varepsilon)$. The term local means with respect to the active sites energy. Thus, local adsorption isotherms are referred to the various groups of active sites corresponding to a particular adsorption energy. The most studied reaction in the field of heterogeneous catalysis, CO oxidation over silica-supported Pt, Rh and $Pt_{0.75}$–$Rh_{0.25}$ alloy catalysts was used as model system.

The experimentally determined local adsorption energies, ε, are defined as the difference between the energy of the minima known as adsorption sites and the average energy of the molecules in the equilibrium bulk state [33]. Their values were relatively high, covering a range from 140 to 280 $kJ\,mol^{-1}$ and they were indicative of a strong interaction between CO and the catalysts surfaces.

The local isotherm values, θ, ranged from zero to one. Their variation against the local adsorption energy ε is shown in Fig. 2 of Ref. [37]. They had a sigmoid form, such as the plots constructed by the method of Adamson and Ling. A short presentation of their method can be found in the monograph by Rudzinsk, Steele and Zgrablich [33]. All isotherms plots had an inflection point around $\theta = 0.5$, and abnormal parts of these plots appeared at lower (Part A) and higher (Part B) ε values. Parts A and C revealed interesting information about the "*topography*" of the active sites on the heterogeneous surface. Similar curves have also been calculated theoretically through Monte Carlo simulations for adsorption on randomly heterogeneous surfaces. The different parts of those plots have been attributed to areas of the surface characterized by different degrees of heterogeneity [38].

The physical meaning of θ values is that lower values ($\theta \to 0$) are indicative of a patchwise topography corresponding to weaker adsorbate–adsorbent interactions. In contrast, at higher values ($\theta \to 1$) the active sites topography is random and the adsorbate–adsorbent interactions are much stronger. These conclusions were ascertained in a subsequent work (c.f. Fig. 8 of Ref. [39]).

Another parameter of significant chromatographic and catalytic importance, determined by the novel methodology of RF-IGC, is the total amount of injected adsorbate present on the adsorbent's surface, C_s^{tot}. This has been determined by integration, from the areas of the plots of θ against adsorbate's local surface equilibrium concentration, C_s^*. Thus, the % uptake of the injected CO is estimated from the estimated C_s^{tot} values and the known amount of injected CO at the experimental conditions of P and T [40]. Similar conclusions have also been drawn from the local monolayer capacities, $C_{\max}^*$, corresponding to potential energy maxima, extracted from Fig. 3 of Ref. [39] and given in Table 2 of the same work. The found $C_{\max}^*$ values were different for every catalyst and increased with the amount of Pt in the catalyst in agreement with the general observation that CO is mainly adsorbed on Pt sites.

Another parameter determined by the novel methodology is the lateral interaction energy, β, which can give important information for the nature of the active sites and their *topography*. The physical meaning of negative β values is that they indicate repulsive surface interactions, while positive β values are indicative of lateral attractions [33]. Lateral *attractions*, ascribable to van der Waals forces, are relatively weak in comparison to chemisorption energies, and in chemisorption, *repulsion* effects are more important. These can be of two kinds: a *short-range repulsion* between the electron clouds of adjacent CO adsorbed molecules or a *long-range repulsion* due to a dipole field. The adsorption of CO molecules on the minima of potential energy (A sites) is accompanied with repulsive forces, which decrease and become zero at monolayer surface coverage. Short-range lateral repulsion affects only nearest neighboring molecules, at high surface coverage values ($\theta \approx 1$), as if the spacing between sites is small. Long-range lateral repulsion affects carbon monoxide molecules, also at high surface coverage but at lower $\theta < 1$ values. Neighboring sites will be occupied more often than the statistical expectation if the situation is energetically favored (β positive → "*patchwise*" topography).

The energy distribution functions, estimated by means of the novel methodology, have given useful information about the "*topography*" and the nature of the active sites on the catalyst surface, similar to other experimental techniques, as thermal desorption spectroscopy studies of the adsorption of CO on group VIII noble metal surfaces [21]. The graph of the energy distribution function, $\varphi(\varepsilon;t)$ versus adsorption energy, ε values is usually described as the "*topography*" of the surface. Such distributions for the adsorption of carbon monoxide over the three studied catalysts are shown in Fig. 4.

In all cases, these curves had a purely Gaussian shape, which is an experimental finding and not an assumption. They cover a wide range of ε values and they present some abnormalities at higher and lower ε values respectively, due to areas of the surface characterized by different degrees of heterogeneity. The found, by means of RF-IGC, energy distribution functions suggested the existence of three groups of active sites. The physical meaning of the three groups of active sites was correlated to the information of thermal desorption spectroscopy studies for the adsorption of CO on group VIII noble metal surfaces: (i) Group A active sites corresponded to high values of coverage and adsorption energy, indicating CO chemisorption on the minima of potential energy of the surface. The topography of these active sites was random, as the values of the lateral interaction energy, β, were negative. Group A active sites correlated to β states of TDS, arising from CO dissociative adsorption. (ii) Groups B and C of active sites corresponded to the molecular adsorption of CO at sites of lower energy and surface coverage. They were characterized by positive values of β, which means that they had a patchwise topography. New adsorption sites can be created by lateral interactions with already adsorbed molecules and a fraction of CO molecules may bound to chemisorbed CO molecules (Part B). Group C active sites cor-

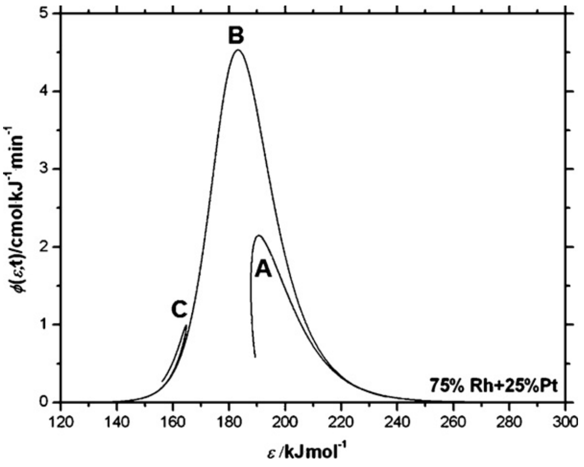


Fig. 4. Indicative plots of the energy distribution function $\varphi(\varepsilon;t)$, versus the local adsorption energy, ε ($kJ\,mol^{-1}$), for the adsorption of carbon monoxide on a bimetallic silica-supported $Pt_{0.25}$–$Rh_{0.75}$ catalyst, at 698 K.

responded to higher β values, in comparison with B group active sites. They were indicative of CO island formation. The bonding of CO on these sites was less strong. Group C active sites were associated with a reconstruction of the surface. The B and C groups of active sites correlated to α states of TDS.

In order to have a clearer picture of the topography and lead in safe conclusions concerning the nature of the adsorption sites the resolution of the various groups of active sites would be useful. In a following work the effect of hydrogen in the "*topography*" of the active sites related to CO adsorption was studied [39]. This study was focused on CO adsorption on Rh/SiO_2 catalyst, at 90 °C and answers to the following questions were given: (1) what amount of molecules is adsorbed on the surface, (2) where are the molecules on the surface, and (3) which is the nature of the surface chemical bonds. It should be noted that a drastic increase of catalysts adsorptive capacity at H_2-rich conditions had been already experimentally confirmed [29] and thus it was expected that hydrogen may drastically affected the topography and the nature of the catalysts active sites.

By plotting the energy distribution function $\phi(\varepsilon;t)$ against the local equilibrium concentration, c_s^*, as shown in Fig. 5, the various groups of active sites were clearly resolved.

It became obvious that quantitative information concerning the effect of H_2 on CO adsorption over the studied catalyst as well as the adsorptive capacity of the various groups of active sites is possible by these plots. However, the most interesting observation, from the plots of Fig. 5, concerned group A of active sites, which in the absence of hydrogen were attributed to CO chemisorption. The intensity and the amount of CO molecules (as indicated by peak area) bound on group A active sites drastically decreased and under H_2-rich conditions group A almost disappeared. This observation partially explained previous kinetic observations that in excess of H_2 the increased rate of CO binding is accompanied by the weakening of its strength [30]. Moreover, it became clear that hydrogen strongly affects the "topography" of the studied solid adsorbent resulting in homogeneity: four groups of active sites: A, B, C and D were observed in the absence of hydrogen. Three groups of active sites (A, B and C) were resolved in H_2-dilute conditions (25% H_2), while C and D groups observed in the absence of hydrogen formed one group. Moreover, under H_2-rich conditions group A sites almost disappeared and groups B, C and D gradiently formed only one group of active sites (B). The latter provided a first indication of the similar properties of groups B and particularly C and D, which in the absence of hydrogen were attributed to lateral interactions with already adsorbed molecules and CO molecules binding over chemisorbed CO molecules.

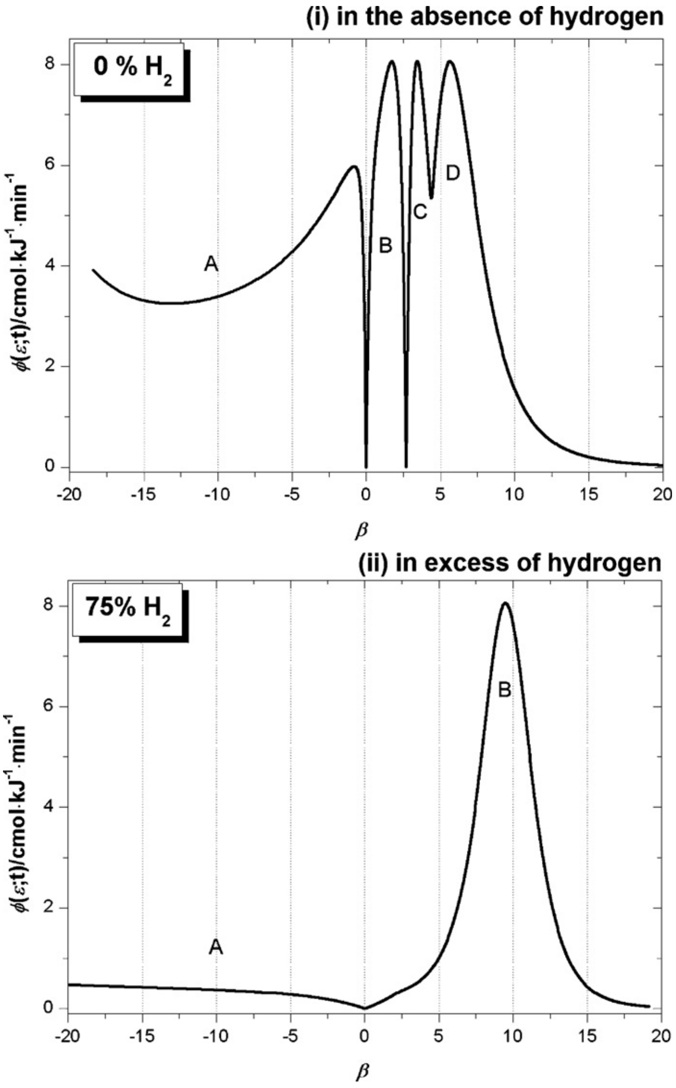


Fig. 6. Comparative presentation of the energy distribution function $\varphi(\varepsilon;t)$ against the lateral interaction energy β for CO adsorption on Rh/SiO_2, at 90 °C, (i) in the absence of hydrogen (0% H_2) and (ii) in excess of hydrogen (75% H_2).

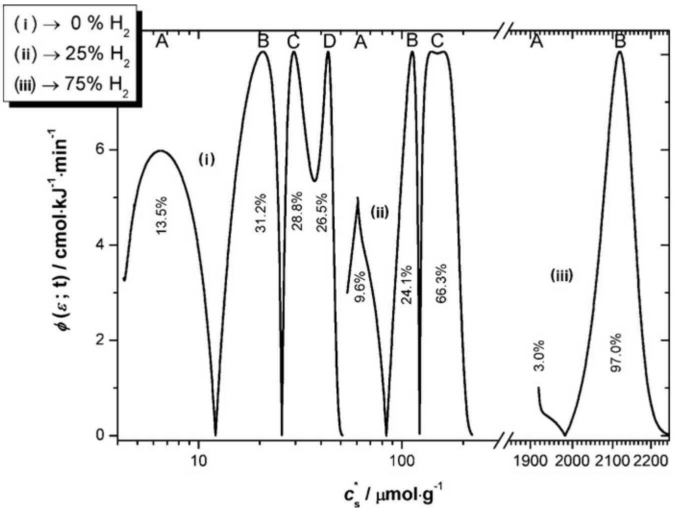


Fig. 5. Semi-logarithmic plots of the energy distribution function $\varphi(\varepsilon;t)$ versus the local equilibrium adsorbed concentration c_s^* of CO on Rh/SiO_2, at 90 °C, (i) in the absence of H_2, (ii) in dilute H_2 and (iii) under H_2-rich conditions.

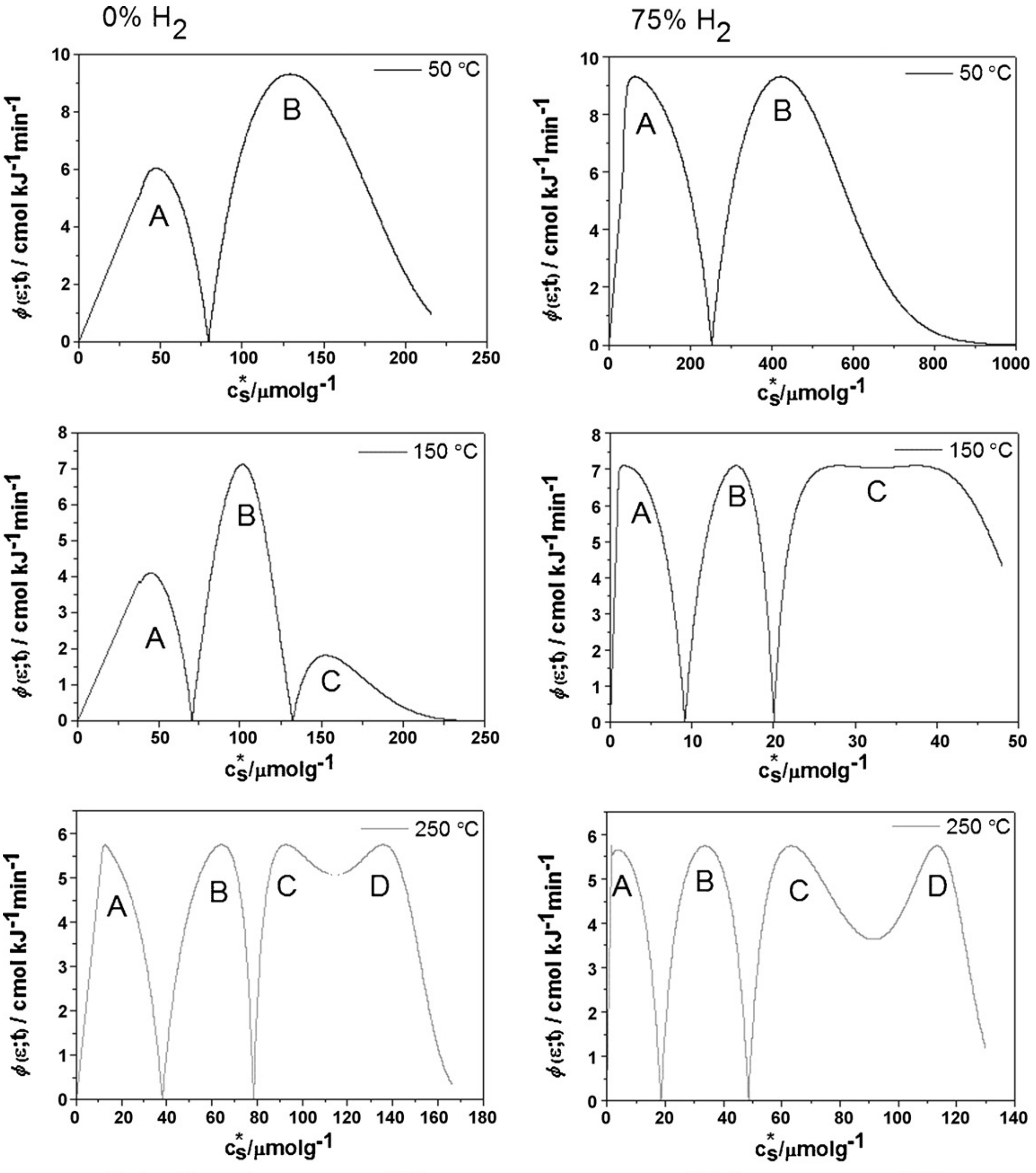
Clear resolution of the various groups of active sites was also achieved by plotting $\varphi(\varepsilon;t)$ against lateral interaction energy, β, as shown in Fig. 6. Similarly to the plots of Fig. 5, various groups of active sites (A, B, C and D) were observed in the absence of hydrogen, while only two (A and B) were resolved under H_2-rich conditions. In addition, under H_2-rich conditions the adsorption of CO over group A active sites was negligible and B, C and D groups of active sites gradiently formed only one group of energy sites (B) which peak was shifted at higher β values.

These plots indicated that in the absence of H_2, the probability of CO chemisorption (Group A sites) was lower compared to that in groups B, C and D in accordance with the fact that chemisorption is an activated process enhanced at higher temperatures. In contrast, under H_2-rich conditions the probability of CO chemisorption became negligible. This fact did not excluded that an amount of CO is chemisorbed but that the vast majority of CO molecules present at the catalyst surface are bound at active sites with the properties of group B. These findings were in agreement with ultra-high vacuum studies on noble metal crystals in which it was concluded that the coadsorption of CO and H_2 produces both mixed CO/H islands with CO adsorbed primarily in bridge positions, as well as repulsive CO–H interactions leading to separated islands [39].

Summarizing the findings of this work [39], it was observed that the topography of Rh/SiO_2 catalyst consisted of both randomly and islands of CO bound over chemisorbed CO molecules, in the absence of hydrogen. In contrast, under H_2-rich conditions, the active sites topography was almost entirely patchwise, ascribed to long-range lateral attractions between adsorbate molecules. In excess of hydrogen, CO adsorption was shifted at higher lateral attractions values which correspond to weaker adsorbate–adsorbent interactions and lower surface coverage. This finding provided an indication of a H_2-induced desorption, which may explain the well-known in the literature enhancement of preferential CO oxidation rate by H_2.

The novel methodologies of RF-IGC were further extended in studying the effects of hydrogen and temperature in CO adsorption over nanosized Au/γ-Al_2O_3 catalysts [40]. Answers to the following physicochemical questions related to the catalytic properties of nanosized gold were given: (1) What amount of CO molecules is adsorbed on the Au catalyst surface? (2) Where are the molecules on the surface? (3) Which is the nature of the surface chemical bonds? (4) Which are the reasons of the extraordinary activity of supported nanosized gold particles concerning low temperature oxidation of CO?

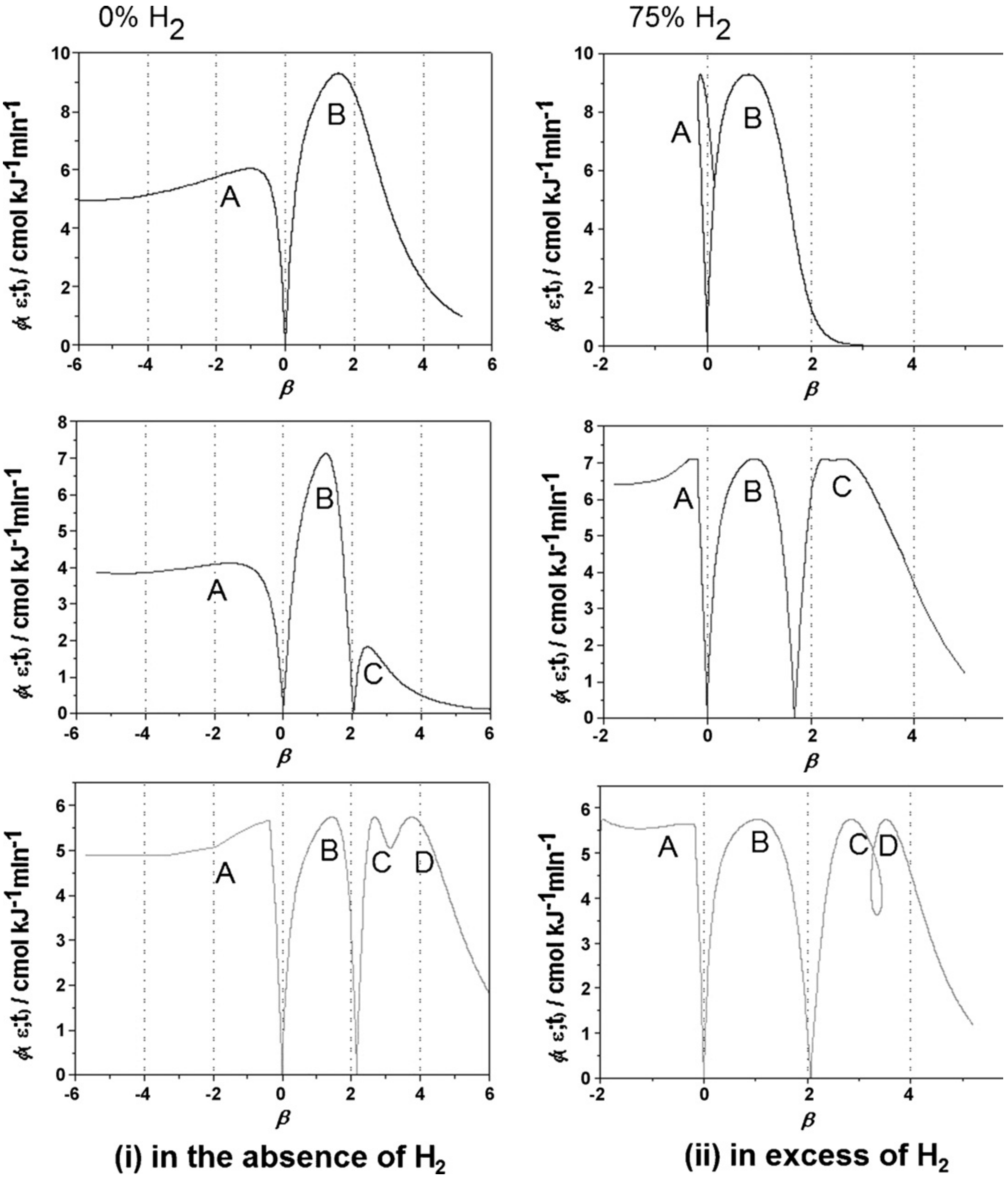
It was concluded that higher amounts of CO can be bound on the catalyst active sites, at conditions compatible with the operation of PEM-FCs. Moreover, at rising temperatures, catalyst adsorptive capacity decreased, as observed in Fig. 7. The degree of surface heterogeneity increased with rising temperature since new groups of



(i) in the absence of H_2

(ii) in excess of H_2

Fig. 7. Semi-logarithmic plots of the energy distribution function $\varphi(\varepsilon;t)$ versus the local equilibrium adsorbed concentration c_s^* of CO on Au/γ-Al_2O_3, at 50, 150 and 250 °C, both (i) in the absence of H_2 and (ii) under H_2-rich conditions.



(i) in the absence of H_2 (ii) in excess of H_2

Fig. 8. Comparative presentation of the energy distribution function $\varphi(\varepsilon;t)$ against the lateral interaction energy β for CO adsorption on Au/γ-Al_2O_3, at 50, 150 and 250 °C, (i) in the absence of H_2 and (ii) under H_2-rich conditions.

active sites appeared, both in the presence as in the absence of hydrogen. The topography of Au/γ-Al_2O_3 catalyst concerning selective CO oxidation was patchwise at lower temperatures and became intermediate at higher temperatures.

The experimentally observed high-activity of Au/γ-Al_2O_3 for selective CO oxidation at ambient temperatures was explained, from Fig. 8 plots, as consequence of CO weaker bonding over most probably metallic Au actives sites in comparison to stronger CO bonding which can take place at active sites located on γ-Al_2O_3 support and which is related to deactivation. On the other hand, strong bonding of CO, observed in the absence of hydrogen, probably due to CO adsorption on active sites of cationic Au^{x+} near the alumina support. The results of the present study suggested that the well-known mild CO bonding over Au/γ-Al_2O_3, which is the basis of catalysis by gold, is more affected by temperature than the presence of hydrogen.

Summarizing, following the initial application of RF-IGC to CO adsorption over Pt–Rh alloy catalysts, the successful investigation of CO adsorption on a quite different in properties solid such as nanosized Au ascertained that the novel methodology of RF-IGC can be used for studying any type of adsorbate–adsorbent interactions.

Other topics studied by similar methodologies of RF-IGC, also utilizing well-studied Pt–Rh alloy catalysts are: local adsorption isotherms on heterogeneous surfaces [41], surface diffusion coefficients for physically adsorbed or chemisorbed species on heterogeneous surfaces [42,43], the standard free energy of adsorption and its probability density function, together with the geometrical mean of the London parts of the total surface free energy $(\gamma_1^L, \gamma_1^L)^{1/2}$ of the adsorbed probe and the solid surface [44], the competition between mass transfer and kinetics of solid catalysts [45] and adsorption entropy, Gibbs free energy, and enthalpy for the adsorption of gases on heterogeneous surfaces [46].

In addition adsorption studies concerning oxidation, hydrogenation and isomerisation reactions over various catalytic systems have been carried out by other groups utilising RF-IGC methodologies [47–51]. The hydrogenation of 1-butene was studied and kinetic information for the elementary steps of adsorption, desorption, and surface reaction over nanosized Pd/ZnO catalysts was obtained [48]. The catalytic/adsorptive properties of ZnO thin films, partially covered with nano-particles Pd or Au, have been also investigated. The entropy of adsorption and other physicochemical quantities were experimentally determined and information for the mechanism of the studied processes and the topography of the studied thin films were extracted. In addition the standard deviation of the kinetic constants was calculated [49]. Moreover, adsorption phenomena taking place on heterogeneous solids were studied, providing information for the nature and the strength of the adsorbate–adsorbent as well as the adsorbate–adsorbate interactions and details of the topography of the active sites [50]. Furthermore, a correlation between adsorption and catalysis has been carried out in the case of NiO and Co_3O_4, by RF-IGC methodologies [51].

5. Conclusions

RF-IGC methodologies are technically simple and combined with suitable mathematical treatments which give the possibility for reliable surface studies providing information for the kinetics of catalyzed surface reactions as well as the topography and the nature of the active sites. The potential of RF-IGC has been evaluated by utilising as model systems CO adsorption/oxidation over, prepared and characterized by Nieuwenhuys and his coworkers, Pt–Rh/SiO_2 and nanosized-Au/γ-Al_2O_3 catalysts.

The main findings or RF-IGC are in agreement with those of other groups utilizing other experimental techniques or theoretical methods and permit insights on the topography and the nature of the active sites. Although IGC has been widely utilized for catalysts characterizations and surface heterogeneity studies [7,14,15,47–52] and references there in] surface catalytic studies giving information for the topography and the nature of the active sites by other IGC methods are not known.

In any case RF-IGC methodologies should be further extended and evaluated in studying other reactions and catalytic systems. Future studies should be more focused on the standard free energy of adsorption and the geometrical mean of the London parts of the total surface free energy, as well as in the thermodynamic parameters ΔS, ΔG and ΔH which are well-studied topics by other groups permitting comparisons and possible improvements. Moreover, a new methodology of RF-IGC permitting, for first time, the estimation of partition functions for adsorbed species on heterogeneous surfaces is under development.

Acknowledgments

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