Time distribution of adsorption active sites on heterogeneous solid surfaces through experimental measurements of adsorption energies, local adsorption isotherms and the energy distribution function by reversed-flow gas chromatography

Research Team

Fani Roubani – Kalantzopoulou, *Professor, National Technical University, Athens, Greece*

Sofia Margariti, Ioannis Bassiotis, Vassilios Siokos, (Research Students) , *National Technical University, Athens, Greece*

Introduction

The Reversed Flow – Gas Chromatography (RF-GC) is a well known dynamic method combining simplicity with accuracy Katsanos [5] and Katsanos et al. [6]. This method is useful especially for complex systems, where surface heterogeneity plays a very important role and must be taken into account in the physicochemical interpretation of the adsorption process, Metaxa et al.[13], Kalogirou et al.[3]. This method based on two mass-balance equations, one in the gas region and the other in the solid bed one, is useful for evaluating adsorption isotherms because it gives model-independent results, Sotiropoulou et al. [20]. The RF-GC method is also described and evaluated for the determination of many physicochemical parameters in homogeneous gas phase, Roubani-Kalantzopoulou et al.[14] and in heterogeneous as well, Yun et al. [22], Karagiorgos et al. [4] and Birbatakou et al. [1].

The RF-GC method has been applied recently for the measurement of some local parameters concerning adsorption energies, ε, with respect to time, Katsanos et al.[7,8], gaseous adsorbate concentrations above the solid surfaces, c_y, local monolayer capacities, c_{max}^*, that is the maximum adsorbed concentrations of the probe gases on the collection of the adsorption sites i being active at time t and local adsorption isotherms, $\theta_i(p,T,\varepsilon)$, Roubani-Kalantzopoulou et al. [15]. In addition, the probability density function, $\varphi(\varepsilon)$, Roubani-Kalantzopoulou et al. [16] (a modified function, of the former $f(\varepsilon)$, Katsanos et al.[9] and Siokos et al. [19], of adsorption energies for some probe gases on heterogeneous solid surfaces, as well as the lateral molecular interaction energies (dimensionless), $\beta\theta_i$, have been determined through the same experimental results, Katsanos et al.[10]. The term ''local'' means with respect to time, that is involves only a limited collection of adsorption sites active at time t.

This article concerns adsorption occurring at gas-solid interfaces, when the solids are heterogeneous in nature, as well determination of adsorption energies and related parameters of seven gaseous substances (five organic in the presence or not of an

inorganic, O_3 or NO_2) on ten heterogeneous solid adsorbents. Thus, a time resolved chromatographic study is done for the characterization of all these gas-solid interfaces.

Experimental

The experimental set-up and the procedure can be found in the invited review article written recently by Roubani- Kalantzopoulou [17].

The light hydrocarbons, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and 1-C_4H_8, as well as the nitrogen dioxide, were obtained from Air Liquide and had a purity of 99.000%-99.999%. The carrier gas was nitrogen 99.999% from Air Liquide, dried by silica gel. Ultra-high-purity hydrogen from the same company was also used as reactant as well as carrier gas for the study of heterogeneous catalytic reactions.

The O_3 was prepared in the laboratory by using a laboratory ozonizer (Ozoneur OZ1-L of OZONIA Int.) and had a concentration of 3.3 g/Nm^3.

The solids Cr_2O_3, CdS, TiO_2 and PbO_2 were pro-analysis products of Merck. The solids ZnS, CaO, MgO and SiO_2 were products of Fluka with a high purity (>99%).

The catalysts used in catalytic studies were NiO black from Fluka (nickel content: ~76%), and Co_3O_4 from Merck (cobalt content: ~80%).

Theory

The RF-GC method does not depend on analytical or numerical solutions of the classical integral Eq. (1) (cf. Refs Margariti et al. [11,12]), Tylipaki et al.[21], Roubani-Kalantzopoulou et al. [17], but on a time function of the extra chromatographic peaks obtained by short flow-reversals of the carrier gas, as Eq. (2) shows:

$$\Theta(p,T) = \int_0^\infty \theta_i(p,T,\varepsilon) f(\varepsilon) \, d\varepsilon \tag{1}$$

$$H^{1/M} = gc(l',t) = \sum_{i=1}^4 A_i \exp(B_i t) \tag{2}$$

where $\Theta(p,T)$ is the overall experimental adsorption isotherm, $\theta_i(p,T,\varepsilon)$ the local isotherm, $f(\varepsilon)$ the probability density function for the adsorption energies, H is the peak height, M the response factor of the detector, A_i the pre-exponential factors, and B_i the exponential coefficients of time t, when flow reversals were performed.

The main equation of the experimental technique as well as of the corresponding model is Eq. (2). The relevant mathematical model with the calculation of A_i and B_i values from the experimental points H, t, and their physical content have been reported many times.

Finally, the necessary relations for the calculation of ε, c_{max}^*, $\theta_i(\theta_t)$, $\varphi(\varepsilon)$ and β from Eq. (2), for the adsorption of gases on heterogeneous surfaces as a function of time, have been obtained through the combination of Eq. (2) and the Jovanovic isotherm model written in the form as Eq. (10) of Ref. [7] shows:

$$\theta(p,T,\varepsilon)=1-\exp(-K\,p) \tag{3}$$

where

$$K = K^{0}(T)\exp(\varepsilon/RT) \tag{4}$$

R being the gas constant, and

$$K^{0} = \frac{h^{3}}{(2\pi m)^{3/2}(kT)^{5/2}}\cdot\frac{\upsilon_{s}(T)}{b_{g}(T)} \tag{5}$$

Here, K is the Boltzmann's constant; m the molecular mass of the adsorbate, h the Planck's constant and $u_{s}(T)/b_{g}(T)$ the ratio of two partition functions, namely the one for the adsorbed molecule, $u_{s}(T)$, and that for the rotations-vibrations in the gas phase $b_{g}(T)$. This ratio equals approximately one.

More precisely, the relations for the calculation of ε(kJ mol^{-1}), c^{*}_{max} (mol g^{-1}) and θ_{t} from experimental data are given by Eqs (6)-(8):

$$\varepsilon = RT\left[\ln\left(KRT\right)-\ln\left(RT\right)-\ln K^{O}\right] \tag{6}$$

$$c^{*}_{max} = c^{*}_{S} + \frac{1}{KRT}\cdot\frac{\partial c^{*}_{S}}{\partial c_{y}} \tag{7}$$

$$\theta_{t} = 1 - \frac{1}{c^{*}_{max}}\cdot\frac{1}{KRT}\cdot\frac{\partial c^{*}_{S}}{\partial c_{y}} \tag{8}$$

According to Jaroniec and Madey [17], the probability density function $f(\varepsilon)$ of Eq. (1) describing the adsorption energy distribution, is defined as the derivative of the number of adsorption sites with respect to the adsorption energy. Since the number of adsorption sites is proportional to the local monolayer capacity c^{*}_{max} of Eq. (7), $f(\varepsilon)$ may be defined as:

$$f(\varepsilon)=\frac{\partial c^{*}_{max}}{\partial\varepsilon}=\frac{\partial c^{*}_{max}/\partial t}{\partial\varepsilon/\partial t} \tag{9}$$

Finally one obtains [23]:

$$f(\varepsilon)=\frac{1}{RT}\left[\frac{KRT\left(\partial c^{*}_{s}/\partial t\right)+\partial^{2}c^{*}_{s}/\partial c_{y}\partial t}{\partial(KRT)/\partial t}-\frac{\partial c^{*}_{s}/\partial c_{y}}{KRT}\right] \tag{10}$$

The modified function $\varphi(\varepsilon)$ is produced if $f(\varepsilon)$ is multiplied by θ and the product divided by c^{*}_{max}.

$$\varphi(\varepsilon;t) = \theta f(\varepsilon)/c^{*}_{max} \tag{11}$$

As regards the lateral interactions of the adsorbed molecules, the dimensionless parameter β Margariti et al.[12] can be obtained:

$$\beta = z\omega / RT \tag{12}$$

ω being the lateral interaction energy and z the number of neighboring atoms for each adsorption site. Thus, the $\theta z\omega$ is the differential energy of adsorption added to ε due to lateral interactions.

Results and discussion

The calculations of the new physicochemical quantities ε, c_{max}^*, θ_t, $\varphi(\varepsilon)$ and β pertaining to heterogeneous surfaces, start from the diffusion bands of RF-GC experiments {cf. Refs [1, 17]} by recording the pairs H, t and calculating the pre-exponential factors A_1, A_2, A_3 and A_4, and the time coefficients B_1, B_2, B_3 and B_4. By entering the pair values of H, t into the DATA lines of a non-linear regression analysis GW- PC program the physicochemical parameters and functions exposed and defined in the section Theory are calculated and printed. The adsorption energy ε versus experimental time, for the systems propylene/chromium oxide and propylene/ozone/chromium oxide (dot line) at 323.2 K, in nitrogen atmosphere is presented in Fig. 1. The gas molecules at time t are exclusively adsorbed on sites i all of the same energy ε_i. The maxima and minima represent rather transition adsorption energies before their final leveling off with time.

The local adsorption isotherm, θ_i, versus adsorption energy, ε_i, for the systems propylene/zinc sulfide and propylene/ozone/zinc sulfide (dot line) at 323.2 K, in nitrogen atmosphere is shown in Fig. 2. The shape of these curves resembles that given by Adamson and Ling, as exemplified by Rudzinski and Everret [18]. The main difference is that, in this case, all the physicochemical quantities are obtained experimentally and not analytically.

Concerning the dependence of distribution function of adsorption energies on the experimental time for the systems ethane/cadmium sulfide and ethane/ozone/cadmium sulfide (dot line) at the same conditions as above, three types of adsorption active sites are evident, Fig. 3. It's impressive that similar results can be carried out from the corresponding plot in Fig. 8, concerning the heterogeneous catalytic hydrogenation of 1-butene on nickel oxide catalytic bed at 260 ^{0}C.

The lateral molecular interaction energy $\beta\theta_i$ (dimensionless) as a function of time for the system 1-butene/(ozone)/silicon oxide in Fig. 5 shows that a similar behavior is observed and the plots also show three kinds of active sites for adsorption. The same results are obtained from the plots in Fig. 4, where a time resolved analysis regarding local isotherms is presented for the system 1-butene/(ozone)/chromium oxide.

The dependence of distribution function of adsorption energies in relation with the adsorption energies themselves for the systems ethylene/magnesium oxide and ethylene/ozone/magnesium oxide at 323.2 K is presented in Fig. 6. A Gaussian curve is observed (the slight deviations from this behavior correspond to the beginning and the end of the experimental results). In Fig. 7, the time resolved analysis of the local monolayer capacities, c_{max}^*, is strongly depending on the experimental temperature.
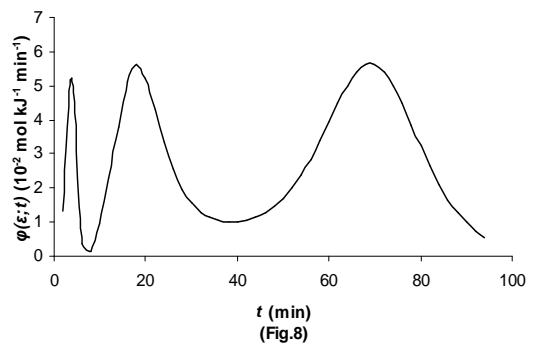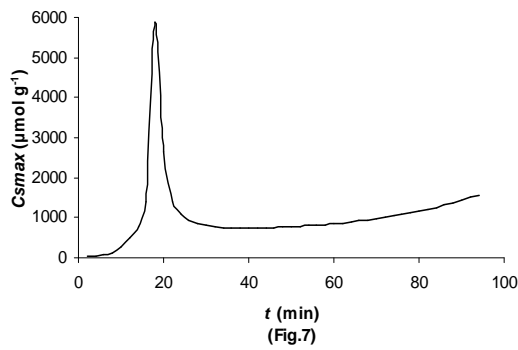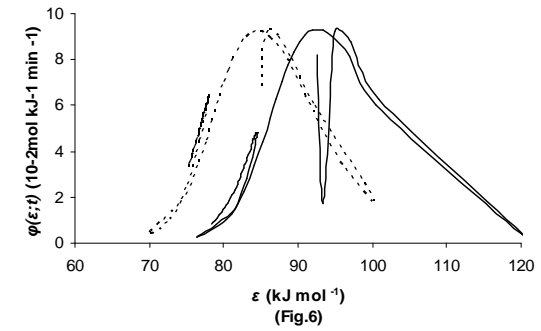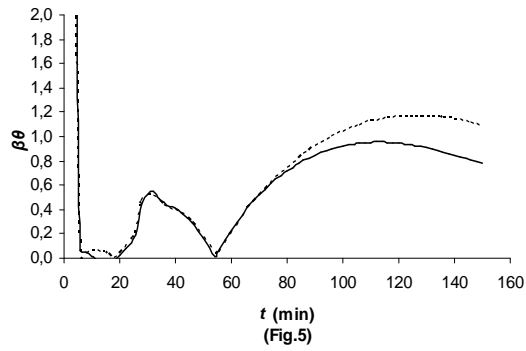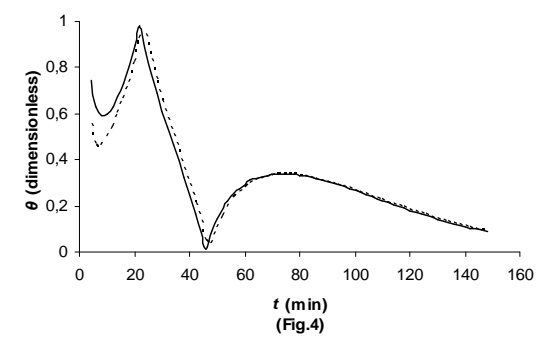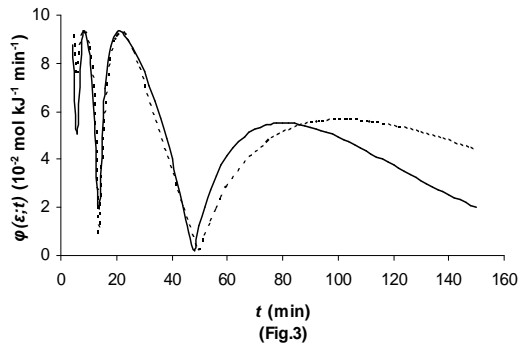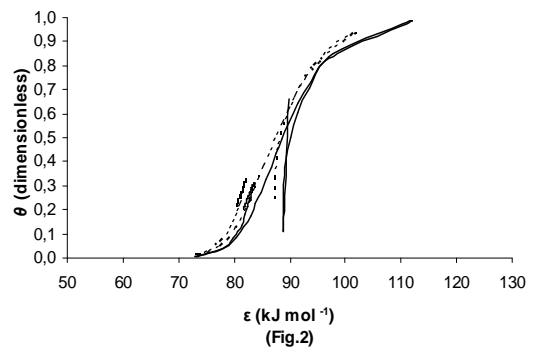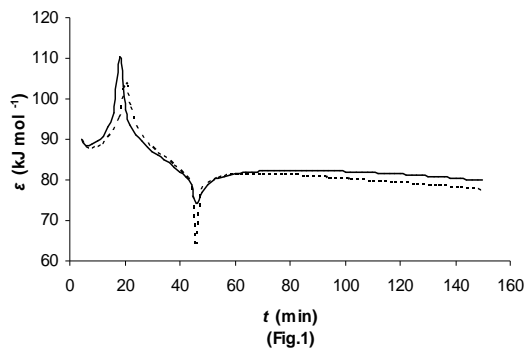
Figures 1-8 . Physicochemical quantities for surface characterization of gas-solid interfaces, through a suitable time -resolved chromatographic analysis.

References
1. Birbatakou, S., Pagopoulou, I., Kalantzopoulos, A. and Roubani-Kalantzopoulou, F. : *J. Chim. Phys.,* **95,** 2180, 1998
2. Jaroniec, M., and Madey, R.: "Physical adsorption on heterogeneous solids", *Elsevier, Amsterdam,* 1998
3. Kalogirou, E., Bassiotis, I., Artemiadi, Th., Margariti, S., Siokos, V. and Roubani-Kalantzopoulou, F.: *J. Chromatogr. A ,* **969**, 81, 2002
4. Karagiorgos, G. and Roubani – Kalantzopoulou, F.: *Z. Phys. Chem,* **203**, 231, 1998
5. Katsanos, N. A.: "Flow Pertubation Gas Chromatography", *Dekker (Marcel), New York, Basel,* 1988.
6. Katsanos, N. A, Thede, R., and Roubani-Kalantzopoulou, F.: *J. Chromatogr. A,* **795**, 133, 1998
7. Katsanos, N. A, Arvanitopoulou, E., Roubani-Kalantzopoulou, F. and Kalantzopoulos, A.: *J. Phys. Chem. B,* **103,** 1152, 1999
8. Katsanos, N. A., Rakintzis, N., Roubani – Kalantzopoulou, F., Arvanitopoulou, E. and Kalantzopoulos, A.: *J. Chromatogr. A,* **845**, 103, 1999
9. Katsanos, N. A., Iliopoulou, E., Roubani-Kalantzopoulou, F., and Kalogirou, E.: *J. Phys. Chem. B,* **103**, 10228, 1999
10. Katsanos, N.A., Roubani – Kalantzopoulou, F., Iliopoulou, E., Bassiotis, I., Siokos,, V., Vrahatis, M. N. and Plagianakos, V. P.: *Colloids and Surface A,* **201,** 173,2002
11. Margariti, S., Siokos, V. and Roubani – Kalantzopoulou, F.: *J. Chromatogr., A,* **1018,** 213, 2003
12. Margariti, S., Bassiotis I. and Roubani-Kalantzopoulou F., *J. Coll. Interf. Sci.,* **274***,* 2004
13. Metaxa, H., Kalogirou, E. and Roubani – Kalantzopoulou, F.: *Russian J. Phys. Chem.,* **73**, 112, 1999
14. Roubani – Kalantzopoulou, F., Kalogirou, E., Kalantzopoulos, A., Metaxa, H., Thede, R., Katsanos, N. A and Sotiropoulou, V.: *Chromatographia,* **46**, 161, 1997
15. Roubani – Kalantzopoulou F., Bassiotis, I., Artemiadi, Th., Margariti, S., Arvanitopoulou, E. and Katsanos, N.A.: *Fresenius Environmental Bulletin,* **10** (No 1), 98, 2001
16. Roubani – Kalantzopoulou, F., Artemiadi, Th., Bassiotis, I., Katsanos, N. A and Plagianakos, V., *Chromatographia,* **53**, 315, 2001
17. Roubani-Kalantzopoulou, F.: *J. Chromatogr. A,* **1037**, 1-2, 2004
18. Rudzinski, W. and Everett. D.H.: "Adsorption of Gases on Heterogeneous Surfaces", *Academic Press, London, chaps*. 4, 5., 1992
19. Siokos, V., Kapolos, J. and Roubani – Kalantzopoulou, F.: *Z. Phys. Chem.* **216**, 1313, 2002
20. Sotiropoulou, V., Vassilev, G. P., Katsanos, N. A, Metaxa, H. and Roubani-Kalantzopoulou, F.: *J. Chem. Soc. Faraday Trans*., **91**, 485, 1995
21. Tylipaki, H., Margariti, S., Bassiotis., I. and Roubani-Kalantzopoulou F.: *Chromatographia*, 59, ¾, 2004
22. Yun, X., Long, Z., Kou, D., Lu, X. and Li H., *J. Chromatogr. A,* **736**, 151, 1996