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New Methodology to Determine the Surface Energy, Specific Interactions and Acid-Base Properties of Titanium Dioxide by Inverse Gas Chromatography

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Abstract

Inverse gas chromatography was used to characterize the thermodynamic surface and interfacial properties of titanium dioxide catalyst. The dispersive component of the surface energy of TiO₂ was determined by using the various models of surface areas of n-alkanes. An excellent linear relation correlating the differential enthalpy and entropy change of adsorption to the carbon atom number was obtained. A new method to separate the polar and non-polar contributions of the enthalpy of adsorption was proposed. The values of polar contributions of differential enthalpy of the probes were classified in increasing order: Benzene<Tetrahydrofuran<Ethyl acetate<Chloroform<Acetone<Acetonitrile<Nitromethane. This order was confirmed by that of the relative polarities of the polar probes. We obtained an interesting linear relation of the polar enthalpy of adsorption versus the relative polarity of molecules. It was proved that the TiO₂ surface exhibits an amphoteric acid base character with stronger basicity. The determination of the specific surface enthalpy and entropy of adsorption allowed to evaluate the acid-base constants of this catalyst. It was proved that the acid constant KA=2.73, the basic constant KD=10.82 and their ratio KD/KA=3.97 clearly showed a catalyst surface rather basic than acidic. The comparison with the results obtained by zetametry confirmed those obtained by inverse gas chromatography. It was proved that the method of the vapor pressure of molecules adsorbed on the Titania surface gave the most accurate acid base constants relative to the methods of molecule polarizability and morphological index of polar and n-alkane molecules.

Keywords: Titania; Surface energy; Enthalpy and entropy of adsorption; Acid base constants; Donor and acceptor number

Introduction

Titanium dioxide, TiO₂, has been widely employed in our lives as the common compound of titanium. Besides titanium (IV) oxide and Titania, TiO₂ is also termed E171 in food coloring and titanium white or pigment white 6 in building paints

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[1-3]. In addition, the powder form of TiO_2 possesses a hydrophilic character [3,4]. Titania embraces various merits and certain optical, electronic and physicochemical properties which makes it convenient for a wide range of applications. TiO_2 is of low cost, available, biologically and chemically inert, stable and corrosion resistant. It is a material of good biocompatibility and strong oxidizing power. In addition, it is efficient as an anti-bacterial agent, in the environmental purification due to its high photocatalytic activity and in the UV protection [2-6]. It seems very interesting to study the physicochemical properties of the Titania catalyst known as Degussa P25. TiO_2 P25 has been extensively used thanks to its high photocatalytic activity. In fact, it was mentioned that it is not easy to find a photocatalyst of greater photoactivity as compared to P25. Based on such information, P25 is described as the ‘de-facto standard titania photocatalyst’ and has been commonly employed as a ‘benchmark’ for photocatalysts. It has been also demonstrated that in several reactions, this mixed-phase Titania exhibited a higher photoactivity than pure anatase. Many papers have been issued on the photocatalytic reactions involving Degussa P25 TiO_2 since 1990 [7-9]. We propose in this paper to determine the surface properties of commercial Degussa P25 TiO_2 particles constituted of 80% anatase and 20% rutile; more particularly, we are interested in the determination of specific interactions of adsorption, Lewis acid base and surface energy of this catalyst by inverse gas chromatography (IGC) at infinite dilution. Organic model molecules were used in this study such as n-alkanes (from n-pentane to n-nonane) and some polar adsorbates such as benzene, chloroform, acetonitrile, nitromethane, ethyl acetate, acetone and tetrahydrofuran. These molecules adsorbed on Titania catalyst allow obtaining by IGC the dispersive component of the surface energy, specific enthalpy and entropy of adsorption and the acid base constants in Lewis terms of TiO_2 .

IGC technique, methods and materials

IGC is the most important technique to characterize the surface properties of solid substrates such as oxides, polymers or copolymers in bulk or adsorbed phases IGC. This powerful technique first used by Conder and Young in 1970’s [10-14] took an important development after 1980 where many researches were devoted to the physicochemical determination of oxides, glass fibers and polymers [15-23].

Polar molecules and n-alkanes of known properties are injected in the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between the organic molecules and the solid, if we suppose that there are no interactions between the probe molecules themselves. Measurements were carried out with a DELSI GC 121 FB Chromatograph equipped with a flame ionization detector of high sensitivity. The retention data were obtained with a stainless-steel column of length 20 cm and 2 mm internal diameter packed with 1 g of titania powders. The net retention volume V_n was calculated by following the same methodology used in other papers [24-26].

On the other hand, the method used to obtain specific enthalpy of interaction between a probe and a solid is that developed by Saint-Flour and Papirer [17-19] who obtained a straight line when plotting $RT \ln V_n$ against $\ln P_0$ where P_0 is the vapour pressure of the probes. In the case of polar probes injected into the column, specific interactions of adsorption ΔG_{sp} can be calculated by using this method.

Polar molecules used to determine the specific interactions with the solid substrates are characterised by their donor (DN) and acceptor (AN) numbers [27]. The acidic K_A and basic K_D constants characterising the solid substrate were calculated by using Papirer et al. method [27]. The dispersive component of the surface energy of solids γ_s^d was determined by using the well-known relationship of Fowkes [28,29].

We used another relation proposed by Dorris and Gray [30] for the calculation of γ_s^d of a solid.

Materials and Solvents

Titania

The titania catalyst was obtained from Degussa in powder form. The titania analysed here, had a specific surface area obtained by BET method by adsorption of nitrogen on titania, 59 m^2/g .

Model organic molecules

Classical organic molecules, characterized by their donor and acceptor numbers [25,29], were used in this study. Corrected acceptor number $AN' = AN - AN^d$, given by Riddle and Fowkes [31] who subtracted the contribution of Van der Waals interactions (or dispersion forces), was used in this paper. We used here the values of AN' and AN' of different polar molecules adopted by Hamieh et al. [24-26].

The different solvents used for IGC measurements were chosen for acid, base and amphoteric properties necessary to determine the acid-base characteristics of the titanium dioxide. All probes (Aldrich) were highly pure grade (i.e., 99%). The probes used were n-alkanes (pentane, hexane, heptane, octane, and nonane); amphoteric solvents: acetonitrile, acetone; basic solvents: ethyl acetate, tetrahydrofuran (THF) and acidic solvent: chloroform and nitromethane.

GC Conditions

The IGC measurements were performed on a DELSI GC 121 FB chromatograph equipped with a flame ionization detector. Dried nitrogen was the carrier gas. The gas flow rate was set at 20 mL/min. The injector and detector temperatures were maintained at 200 °C during the experiments. To achieve infinite dilution, each probe was injected with 1 μ L Hamilton syringes taken from the vapor above the liquid solvent surface and emptied into air, in order to approach linear condition gas chromatography, equipped with a split system. In such a way that the interactions between probe molecules can be considered to be negligible and only the interactions between the surface of the solid and an isolated probe molecule are important. The column temperatures were 40 to 120 °C, varied in 10 °C steps. Each probe injection was repeated three times, and the average retention time, t_R , was used for the calculation. The standard deviation was less than 1% in all measurements. In all experiments, the real retention time was systematically calculated based on the first order retention time taking into account the peak asymmetry. The packed columns were then preconditioned (at a temperature equal 130 °C and under a nitrogen flow rate) overnight to remove any residual solvent left in the packing material.

Results and Discussion

Determination of $RT \ln V_n$ of various solvents adsorbed on the titanium dioxide

Experimental results obtained by IGC measurements allowed giving the values of $RT \ln V_n$ of n-alkanes and polar solvents adsorbed on the titanium dioxide (Table 1).

TABLE 1. Values of $RT \ln V_n$ (kJ/mol) of n-alkanes and polar molecules adsorbed on titanium dioxide as a function of the temperature

Temperature (K) Molecule	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15
C6	4.081	3.257	2.435	1.614	0.794	-0.025	-0.843	-1.660	-2.477
C7	7.986	7.162	6.339	5.517	4.696	3.876	3.058	2.240	1.423
C8	10.768	9.914	9.060	8.208	7.357	6.506	5.657	4.809	3.961
C9	13.735	12.816	11.899	10.982	10.067	9.152	8.239	7.326	6.415
Benzene	6.396	4.939	3.484	2.029	0.576	-0.876	-2.328	-3.778	-5.228
Chloroform	3.020	1.692	0.365	-0.961	-2.286	-3.610	-4.933	-6.255	-7.576
Nitromethane	7.260	5.841	4.423	3.006	1.590	0.175	-1.239	-2.653	-4.065
Acetonitrile	-3.654	-5.384	-7.113	-8.840	-10.57	-12.29	-14.02	-15.74	-17.46
Acetone	0.027	-1.535	-3.096	-4.657	-6.216	-7.77	-9.33	-10.89	-12.44
Ethyl acetate	3.399	1.858	0.319	-1.220	-2.757	-4.294	-5.829	-7.364	-8.897
Tetrahydrofuran	17.432	16.594	15.758	14.922	14.088	13.254	12.422	11.590	10.760

The values given on Table 1 will allow evaluating the dispersive component of the surface energy and the acid-base properties of Titania.

Thermodynamic measurements of adsorption parameters

We calculated the thermodynamics parameters of adsorption of different organic molecules on the titanium dioxide surface. The differential heat of adsorption ΔH_a^0 and the standard entropy change of adsorption ΔS_a^0 of the probe can be obtained from the thermodynamic relations (1) and (2):

$$\Delta H_a^0 = -R \frac{\partial(\ln V_n)}{\partial(\frac{1}{T})} \tag{1}$$

$$\Delta S_a^0 = - \left(\frac{\partial(RT \ln V_n)}{\partial T} \right) \tag{2}$$

The obtained straight lines of $\ln V_n=f(1/T)$ were presented on Fig. 1. A general linear equation was applied (Eq. 3):

$$\ln V_n = \alpha \left(\frac{1}{T} \right) + \beta \tag{3}$$

Where α and β are constants depending on the probe nature.
 One deduced ΔH_0 and ΔS_0 from equation (3):

$$\Delta H_a^0 = -R\alpha; \Delta S_a^0 = -R\beta \tag{4}$$

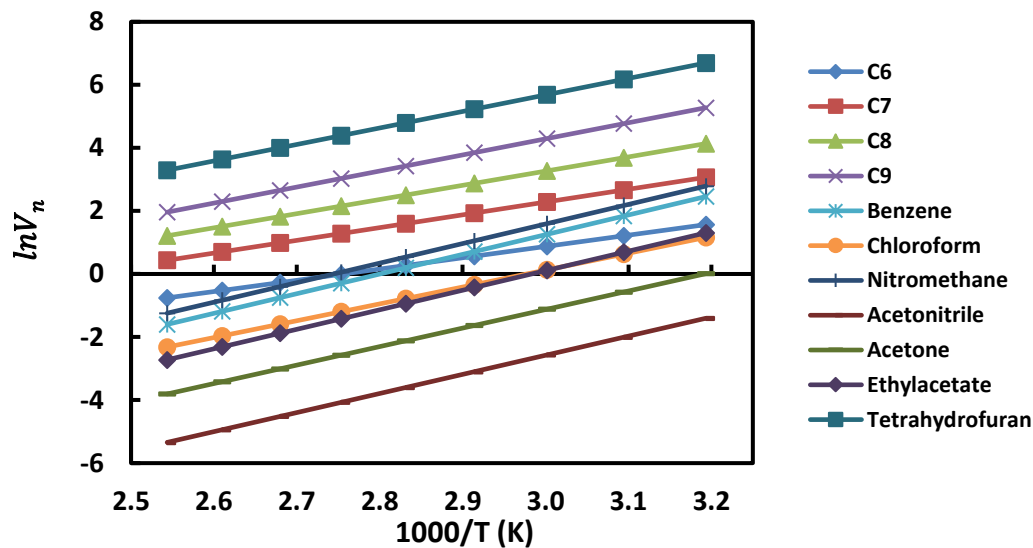


Fig. 1. Values of $\ln V_n$ versus of $1000/T$ of different organic molecules adsorbed on TiO_2 surface.

By using equations (1 to 4), the curves of Fig. 1 allowed to obtain the results presented on Table 1 the differential heat and the entropy change of adsorption.

TABLE 2. Values of the differential enthalpy $\Delta H_a^0(\text{kJ/mol})$, entropy change $\Delta S_a^0(\text{J K}^{-1} \text{mol}^{-1})$ and the equations of free enthalpy $\Delta G_a^0(T) (\text{kJ/mol})$ of different probes adsorbed on TiO_2 particle surface.

Molecules	$\Delta H_a^0 (\text{kJ/mol})$	$\Delta S_a^0 (\text{J K}^{-1} \text{mol}^{-1})$	$\Delta G_a^0(T) (\text{kJ/mol})$
C6	-29.747	-82.0	$-29.747+8.20 \times 10^{-2} T$

C7	-33.677	-82.1	$-33.677+8.21 \times 10^{-2} T$
C8	-37.411	-85.1	$-37.411+8.51 \times 10^{-2} T$
C9	-42.388	-91.5	$-42.388+9.15 \times 10^{-2} T$
Benzene	-51.897	-145.3	$-51.897+14.53 \times 10^{-2} T$
Chloroform	-44.496	-132.5	$-44.496+13.25 \times 10^{-2} T$
Nitromethane	-51.589	-141.6	$-51.589+14.16 \times 10^{-2} T$
Acetonitrile	-50.394	-172.6	$-50.394+17.26 \times 10^{-2} T$
Acetone	-48.840	-155.9	$-48.840+15.60 \times 10^{-2} T$
Ethyl acetate	-51.532	-153.7	$-51.532+15.37 \times 10^{-2} T$
Tetrahydrofuran	-43.550	-83.4	$-43.550+7.34 \times 10^{-2} T$

The differential enthalpy and entropy change of adsorption can be correlated to the carbon atom number n_c . We obtained relations 5 and 6:

$$\Delta H_a^0 \text{ (kJ/mol)} = -4.166 n_c - 4.564 \quad (5)$$

$$\Delta S_a^0 \text{ (J K}^{-1} \text{ mol}^{-1}) = -3.164 n_c - 61.426 \quad (6)$$

ΔH_a^0 and ΔS_a^0 increase negatively when the carbon atom number in the probe increases (Table 2). This increase is due to the increase in the boiling points of n-alkanes and to the stronger interaction between the solute and TiO₂ catalyst surface.

The specific interactions between benzene's π electrons and the TiO₂ surface lead to more negative value of ΔH_a^0 than the corresponding values for n-alkanes with the same carbon atom number. This more important enthalpy is due to the larger interaction between benzene and TiO₂ surface.

The ΔH_a^0 values of polar probes increase from tetrahydrofuran to benzene:

Tetrahydrofuran < Chloroform < Acetone < Acetonitrile < Ethyl acetate ≤ Nitromethane ≤ Benzene

Fig. 2 showed the position of the different n-alkanes and polar molecules in the representation of $\Delta H_a^0 = f(n_c)$, where the n-alkane straight line is relative to the dispersive interactions with the titanium dioxide surface.

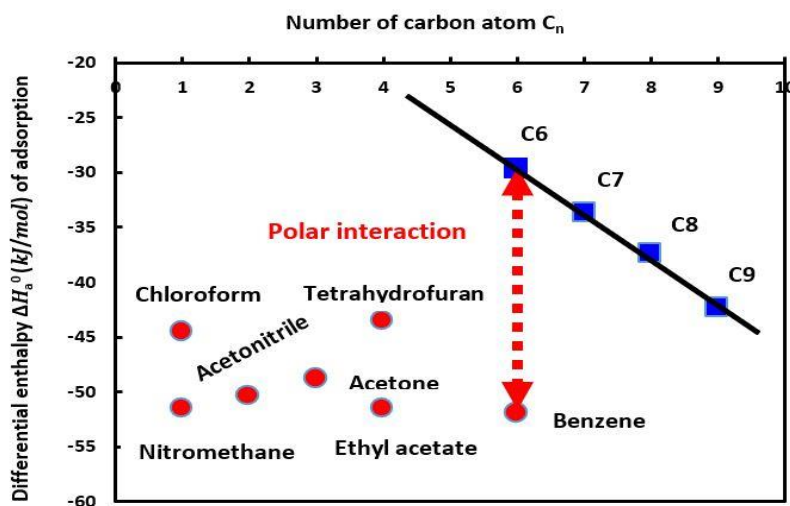


Fig. 2. Values of the differential enthalpy of different organic molecules adsorbed on TiO₂ surface as a function of the carbon atom number in molecules.

When considering equation (4) and the values of polar probes from Table 2, one can deduce the polar and non-polar contributions of every molecule (Table 3).

TABLE 3. Values of polar and non-polar enthalpies $\Delta H_a^{pol.}(kJ/mol)$ and $\Delta H_a^{non-pol.}(kJ/mol)$ of different probes adsorbed on TiO_2 particle surface.

Probes	$\Delta H_a^0(kJ/mol)$	$\Delta H_a^{pol.}(kJ/mol)$	$\Delta H_a^{non-pol.}(kJ/mol)$
C6	-29.747	0	-29.747
C7	-33.677	0	-33.677
C8	-37.411	0	-37.411
C9	-42.388	0	-42.388
Benzene	-51.897	-23.75	-28.147
Chloroform	-44.496	-31.779	-12.716
Nitromethane	-51.589	-42.860	-8.729
Acetonitrile	-50.394	-41.843	-8.551
Acetone	-48.840	-36.338	-12.502
Ethyl acetate	-51.532	-30.306	-21.226
Tetrahydrofuran	-43.550	-28.887	-14.663

The values of polar contributions of the enthalpy of adsorption $\Delta H_a^{pol.}$ of polar probes can be classified in increasing order:

Benzene<Tetrahydrofuran<Ethyl acetate<Chloroform<Acetone<Acetonitrile<Nitromethane

This order is in perfect agreement with that obtained with the relative polarities of the above polar molecules. The polar differential enthalpy of adsorption is another way to describe the polar interaction between the organic molecules and the titanium dioxide catalyst. We presented on Fig. 3 the variations of the enthalpy of adsorption of the probes on TiO_2 surface as a function of their relative polarities (R.P.).

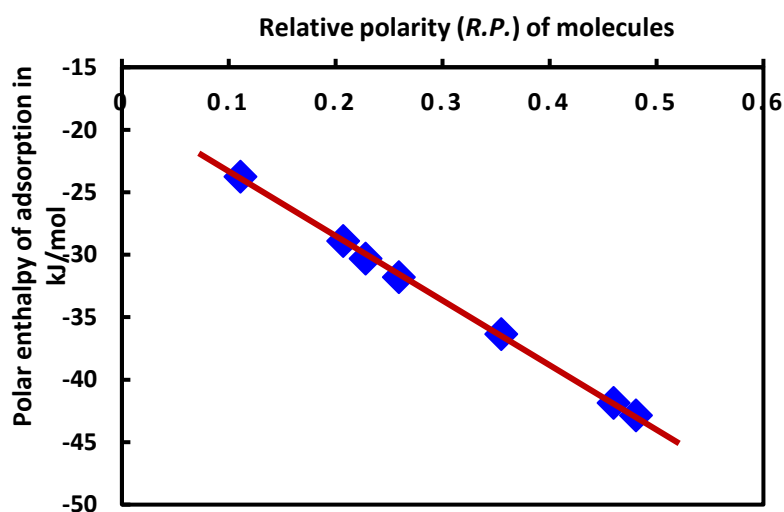


Fig. 3. Variations of the enthalpy of adsorption $\Delta H_a^{pol.}$ (in kJ/mol) of the probes on TiO_2 surface as a function of the relative polarity.

Fig. 3 showed a perfect linear relation given by:

$$\Delta H_a^{pol.} = -51.121 \times R.P. - 18.337; R^2=0.9992 \quad (7)$$

The IGC technique is advantageously proved to be an excellent and simple tool that describes more accurately the physicochemical properties of nanoparticles.

Determination of the dispersive component of the surface energy of titanium dioxide

In order to calculate the dispersive component of the surface energy of TiO₂, we used the various surface areas of n-alkanes using different models the values of the dispersive component of the surface tension $\gamma_l^d(T)$ of n-alkanes as a function of the temperature [32-35].

By plotting $RT \ln V_n$ as a function of $2Na\sqrt{\gamma_l^d}$ of n-alkanes at various temperatures, we obtained the values of dispersive component γ_s^d of the surface energy of TiO₂ for the chosen molecular model. The obtained results are given in Fig. 4 for the different surface area models.

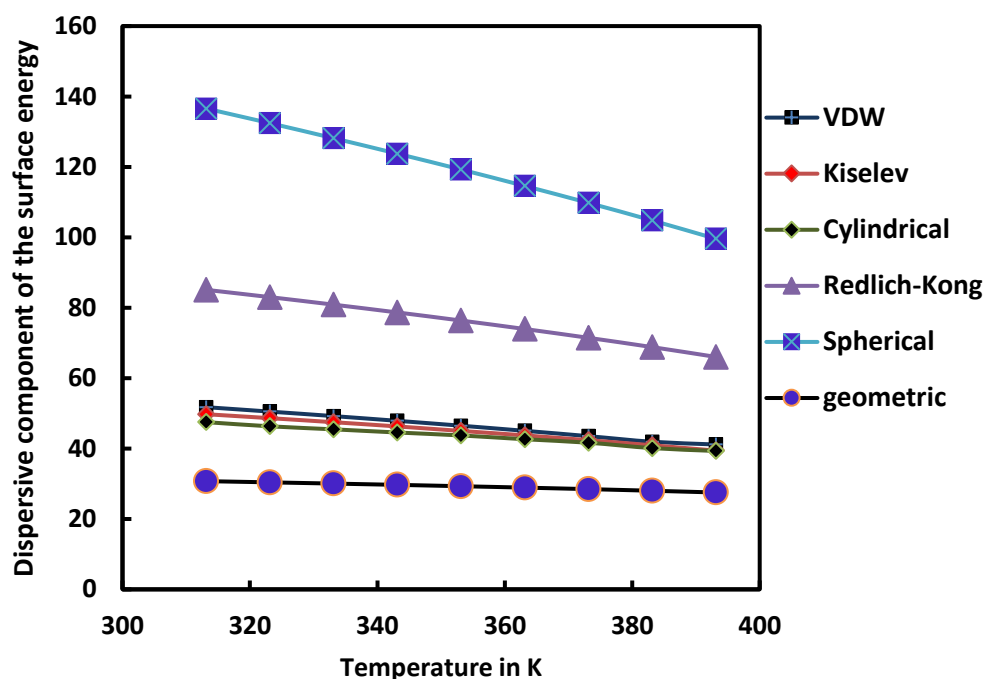


Fig. 4. Variations of the dispersive component of the surface energy γ_s^d (mJ/m^2) of TiO₂ as a function of the temperature T (K) using the different molecular models of n-alkanes surface areas (VDW: Van der Waals model).

The results obtained by IGC using the various molecular models of the dispersive component of the surface energy γ_s^d (mJ/m^2) of TiO₂ and showed in Fig. 4 can be also given as a function of the temperature by the equations in the Table 3.

TABLE 3. Equations $\gamma_s^d(T)$ of TiO₂ for the different molecular models of n-alkanes surface areas, the slope and the extrapolated values $\gamma_s^d(0K)$.

Molecular model	$\gamma_s^d(T)$ (in mJ/m^2)	$\frac{d\gamma_s^d}{dT}$ (in $mJ m^{-2} T^{-1}$)	$\gamma_s^d(T = 0K)$ (in mJ/m^2)	Regression coefficient
VDW	$\gamma_s^d = -0.14T + 94.84$	-0.14	94.84	$R^2=0.9979$

Kiselev	$\gamma_s^d = -0.13T + 90.34$	-0.13	90.34	$R^2 = 0.9975$
Cylindrical	$\gamma_s^d = -0.10T + 79.29$	-0.10	79.29	$R^2 = 0.9953$
Redlich-Kwong	$\gamma_s^d = -0.24T + 159.84$	-0.24	159.84	$R^2 = 0.9977$
Spherical	$\gamma_s^d = -0.46T + 281.67$	-0.46	281.67	$R^2 = 0.9987$
geometric	$\gamma_s^d = -0.04T + 43.36$	-0.04	43.36	$R^2 = 0.9958$

These above equations of $\gamma_s^d(T)$ were obtained for a temperature interval (313.15 K, 393.15 K). We observed an important difference in the behavior of $\gamma_s^d(T)$ of titanium dioxide depending on the various molecular models. We can see this net difference by observing the different values of the slope of $\gamma_s^d(T)$ relative to the molecular model. The most used model by the scientists is that relative to Kiselev results (equivalent to Fowkes method). Van der Waals and Kiselev models here showed similar results of $\gamma_s^d(T)$ with identical slopes followed by the results of the cylindrical model, the different values of $\gamma_s^d(T)$ of TiO₂ catalyst in such cases are comprised between 40 and 52 mJ/m². However, these results are very different from those obtained by the other models (Redlich-Kwong, spherical and geometric models). By extrapolating to the 0 K absolute temperature, we found the extrapolated values of $\gamma_s^d(0K)$ of TiO₂ catalyst for VDW and Kiselev models approaching 90 to 95 mJ/m² whereas they reached 282 mJ/m² for spherical model. It is not surprising that the spherical model is one of the models which is out of trend, because clearly molecules such as alkanes have rather cylindrical than spherical geometry. That is why the cylindrical model is the best-applied model.

These results again proved that the $\gamma_s^d(T)$ values of solids obtained by IGC are not true in a quantitative way but they can be considered interesting as qualitative results by comparison between the different molecular models as we proved it in other studies [24,25].

One of the above results was to choose another method to evaluate the specific interactions and acid-base constants in Lewis terms of TiO₂ catalyst. The Saint-Flour and Papirer method was used to determine the physicochemical properties of the above solid catalyst.

Determination of the specific interactions and acid-base properties of TiO₂ catalyst

The variations of the specific free energy on Fig. 5 we plotted the variations of the specific free energy ($-\Delta G^{sp}$) of TiO₂ catalyst surface in interaction with the different adsorbed polar probes as a function of the temperature T.

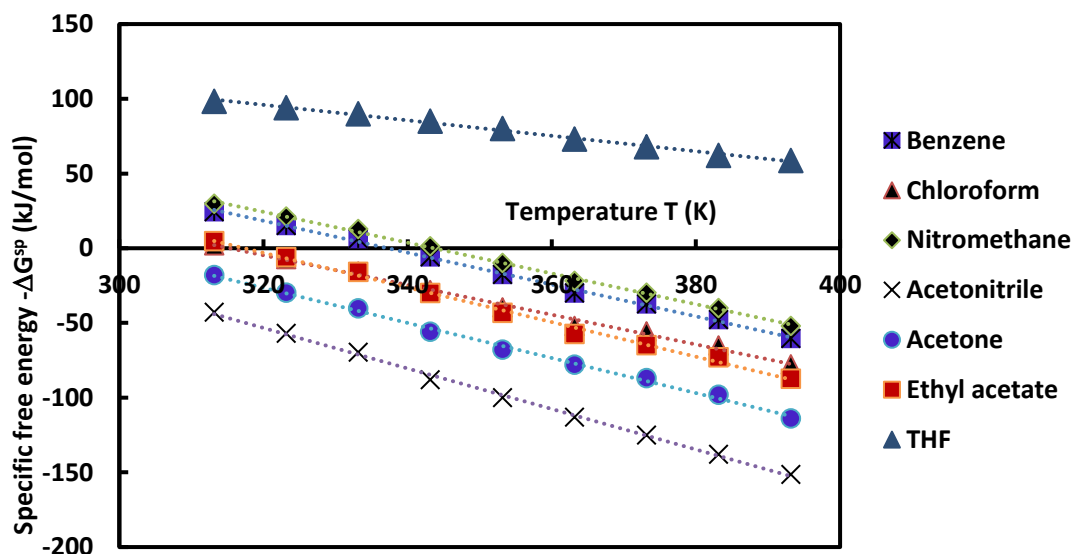


Fig. 5. Evolution of the specific free energy ($-\Delta G^{sp}$) of adsorption of polar molecules on TiO₂ surface as a function of the temperature.

Fig. 5 clearly showed linear dependency of ($-\Delta G^{sp}$) of TiO_2 as a function of the temperature. We deduced from the above different straight lines the values of the specific enthalpy ΔH^{sp} and entropy ΔS^{sp} of adsorption of polar molecules on TiO_2 catalyst. The obtained results are given on Table 4.

TABLE 4. Values of the specific enthalpy ΔH^{sp} and entropy ΔS^{sp} of adsorption of polar molecules on TiO_2 catalyst surface.

Polar probes	$-\Delta H^{sp} (kJ mol^{-1})$	$-\Delta S^{sp} (kJ K^{-1} mol^{-1})$
Benzene	359.49	1.066
Chloroform	313.61	0.995
Nitromethane	354.18	1.031
Acetonitrile	371.79	1.333
Acetone	352.48	1.187
Ethyl acetate	364.31	1.148
THF	261.66	0.518

Determination of the acid base constants of TiO_2 catalyst surface

To determine the acid-base constants K_A and K_D of TiO_2 catalyst surface, we plotted on Fig. 6 the variations of $-\Delta H^{sp}/AN'$ as a function of DN'/AN' of different polar molecules adsorbed on TiO_2 surface.

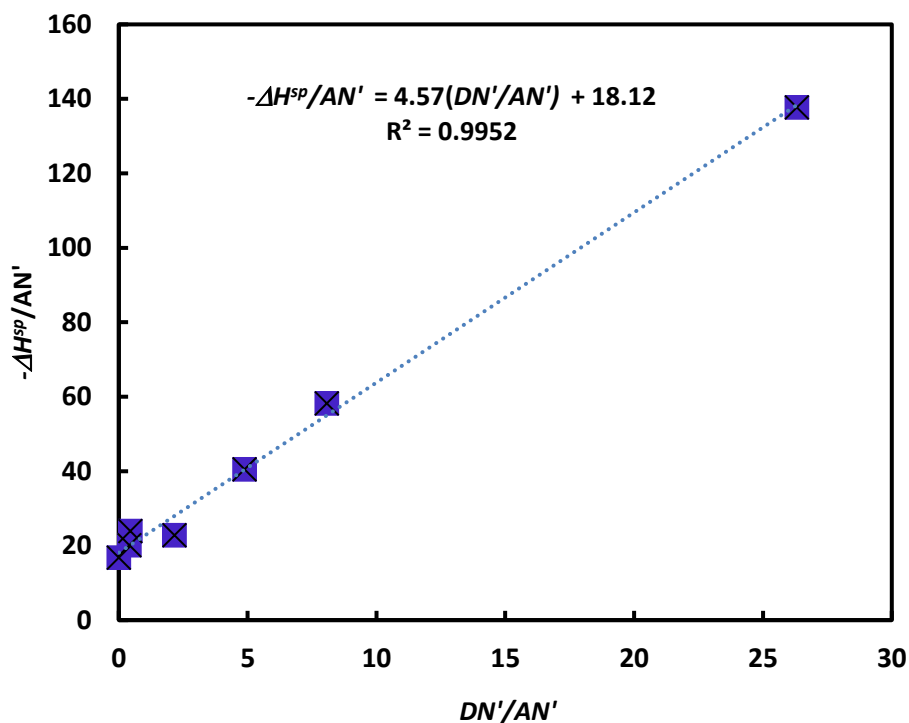


Fig. 6. Variations of $-\Delta H^{sp}/AN'$ as a function of DN'/AN' of different polar molecules adsorbed on TiO_2 surface.

The curve of Fig. 6 is a straight line with an excellent linear regression coefficient ($R^2=0.9952$) and the following relation gives the corresponding equation (8):

$$-\Delta H^{sp}/AN'=4.57(DN'/AN')+18.12 \quad (8)$$

From equation (8), we deduced the acid-base constants K_A and K_D of TiO_2 surface:

$$K_A=4.57 \text{ kJ/mol and } K_D=18.12 \text{ kJ/mol}$$

The constants K_A and K_D can be given in dimensionless parameters by:

$$K_A=2.73, K_D=10.82 \text{ and } K_D/K_A=3.97$$

This study showed the amphoteric acid base character of TiO_2 catalyst with a strong basicity that is equal about fourth times its acidity force.

Comparison with acid-base properties of Titania dispersions in organic media

In a previous paper [36], we studied the acid-base properties of the dispersion of TiO_2 particles in organic medium by using the data obtained by zetametry in organic liquid medium. The method used determines the electron acceptor number and electron donor number of TiO_2 catalyst was that developed by Siffert et al. [37]. Based on this study, Hamieh et al. [36] obtained the following acceptor ANS' and donor number DNS' of the Titania catalyst: $DNS'=46$, $ANS'=11$ and $DNS'/ANS'=4.18$. The comparison of these results with those obtained by IGC leads to the following findings: $DNS'/KD=4.25$, $ANS'/KA=4.03$. It is interesting that both, the acid and base character as well are 4 times bigger in liquid medium than in infinite gas dilution. By comparing the ratio $DNS'/ANS'=4.18$ to that of $KD/KA=3.97$, we deduced that the ratio of the basic character on the acid character in both cases are comparable.

Other methods to determine the acid base properties of TiO_2

Donnet et al. method of deformation polarizability In order to resolve some difficulties in the determination of the acid base properties of solid substrates, Donnet et al. [38] proposed an original method taking into account the deformation polarizability α_0 for the determination of specific interactions between adsorbate and adsorbent. They plotted the variation of $RT \ln Vn$ as a function of $(h\nu_L)^{1/2} \alpha_{0,L}$ for all used probes, where ν_L the electronic frequency of the probe is and h the Planck's constant. Donnet et al. [38] proved the expression (9):

$$RT \ln Vn = K(h\nu_s)^{1/2} \alpha_{0,s} [(h\nu_L)^{1/2} \alpha_{0,L}] + C \quad (9)$$

Where ν_s is the electronic frequency of the solid, $\alpha_{0,s}$ its polarizability and K a constant given by expression (15):

$$K = \frac{3}{4} \frac{N}{(4\pi\epsilon_0)^2} \left(\frac{1}{d_{s,l}} \right)^6 \quad (10)$$

With ϵ_0 the permittivity of the vacuum and $d_{s,l}$ the distance of adsorbate-adsorbent interaction, assumed constant for all probes studied as 0.3 nm. This method is represented by the function $RT \ln Vn = f[(h\nu_L)^{1/2} \alpha_{0,L}]$ and allowed to obtain the specific enthalpy of interaction [38].

By applying the Donnet et al. method, we obtained Fig. 7 showing the evolution of the specific enthalpy of interaction as a function of the temperature of the different polar molecules adsorbed on the titania surface.

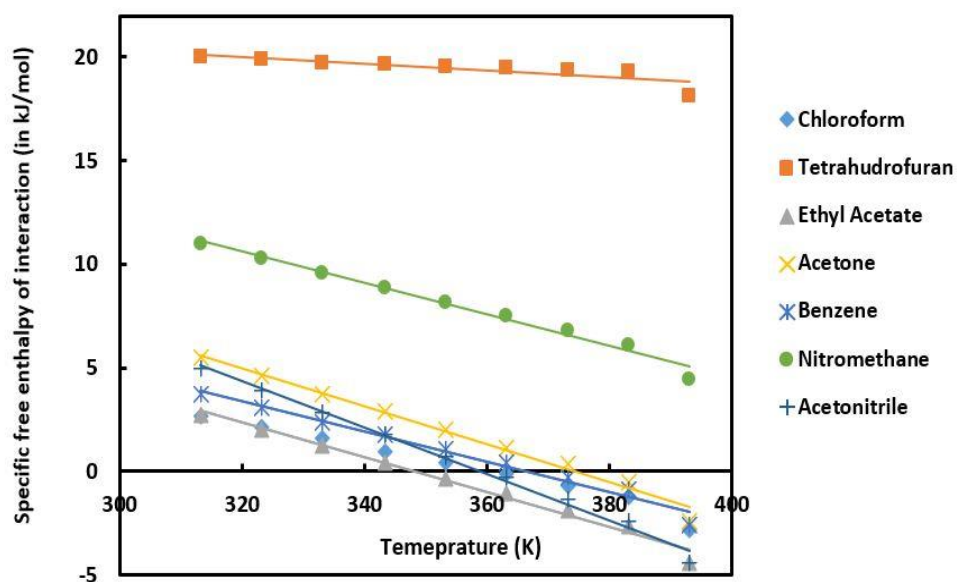


Fig. 7. Variation of the specific free energy ($-\Delta G^{sp}$) (kJ/mol) of adsorption of polar molecules on TiO_2 surface as a function of the temperature by using Donnet et al. method.

Figure showed that THF exhibits the larger interaction with the Titania particle surface, followed by nitromethane and acetone.

The representation of the variations of $(-\Delta H^{sp}/AN')$ as a function of DN'/AN' of different polar molecules adsorbed on TiO_2 surface (Fig. 8) by using the deformation polarizability of molecules led to the values of acid base constants.

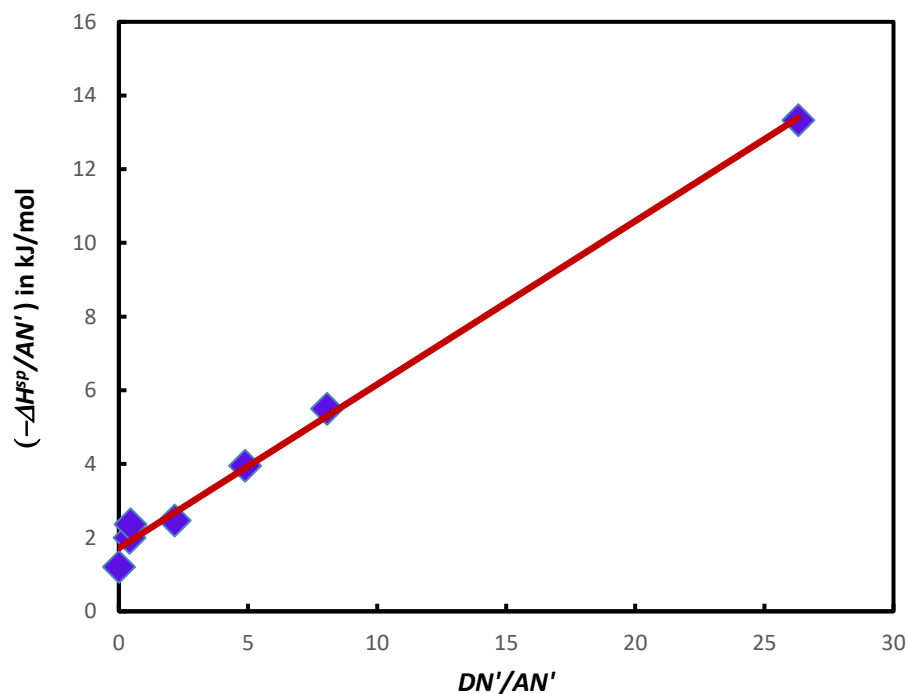


Fig. 8. Variations of $-\Delta H^{sp}/AN'$ as a function of DN'/AN' of different polar molecules adsorbed on TiO_2 surface.

The straight line obtained in Fig. 8 gave relation (11):

$$-\Delta H^{sp}/AN' = 0.444 DN'/AN' + 1.719; R^2 = 0.9947 \quad (11)$$

From the relation (16), we obtained the acid base constants of TiO_2 by the method of the deformation polarizability:

$$K_{A.dp.} = 0.444 \text{ kJ/mol}; K_{D.dp.} = 1.719 \text{ kJ/mol}; K_{D.dp.}/K_{A.dp.} = 3.872$$

The problem of this method is that the values of ν_l and $\alpha_{0,l}$ of n-alkanes and polar molecules are not known with good accuracy and consequently the obtained values of acid base constants cannot be accurately calculated. However, by comparing this method with the previous method of the vapor pressure of molecules, we observed that the ratio K_D/K_A is almost the same in the two cases.

Brendlé-Papirer method of topological index

Brendlé and Papirer [39] proposed another method based on the use of the topological index χ_T of probes represented the variation of $RT \ln V_n = f(\chi_T)$ of n-alkanes, polar molecules, branched alkanes and cycloalkanes. By using the various values of the topological index χ_T of n-alkanes and polar molecules [39,40], we obtained the specific interactions and the acid-base constants. By applying this method on the titanium dioxide particles, we obtained the results presented on Fig. 9.

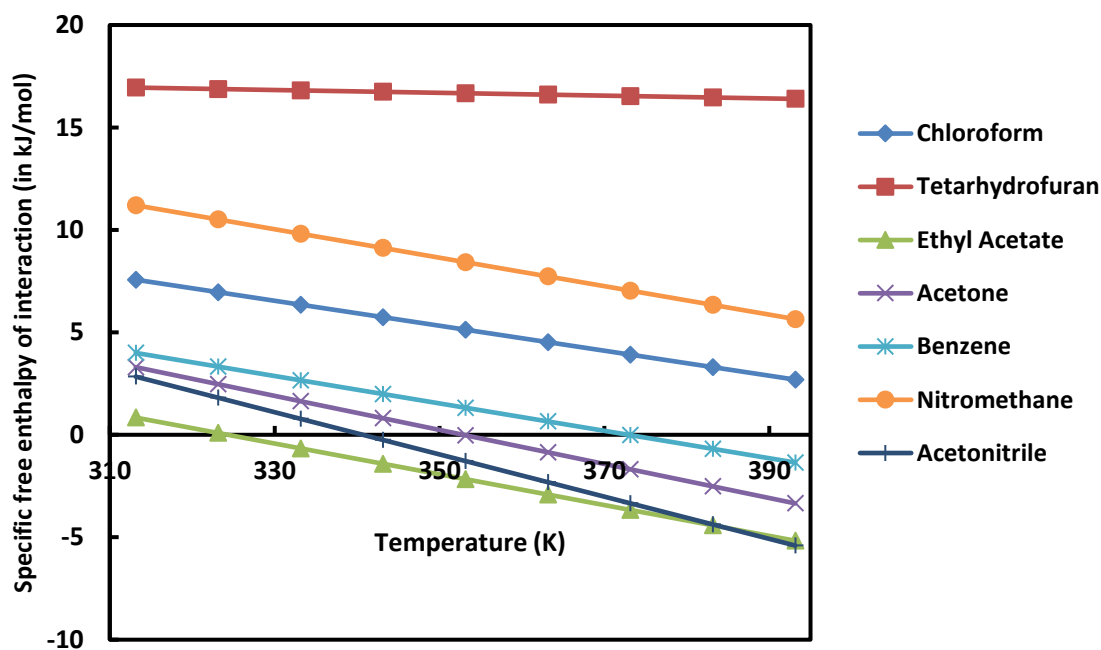


Fig. 9. Variation of the specific free energy ($-\Delta G^{sp}$) (kJ/mol) of adsorption of polar molecules on TiO_2 surface as a function of the temperature by using Brendlé-Papirer method.

Fig. 9 also showed a larger value of the specific free enthalpy for tetrahydrofuran followed by nitromethane. The three used methods gave approximately the same tendency of the comparison between the different polar molecules.

By using the topological index (ti.) of polar molecules, we obtained relation (12):

$$-\Delta H^{sp}/AN' = 0.319 DN'/AN' + 1.746; R^2 = 0.9942 \quad (12)$$

and the acid base constants

$$K_{A.ti.}=0.319 \text{ kJ/mol}; K_{D.ti.}=1.746 \text{ kJ/mol}; K_{D.ti.}/K_{A.ti.}=5.473$$

The ratio K_D/K_A is quite different from the values obtained by the two previous methods. There is no universal method to determine the acid base constants of a solid substrate. However, the method using the concept of vapor pressure seems until know the more appropriated method that takes into account the variation of the vapor pressure versus the temperature and the resulting effect on the calculation of the specific thermodynamic variables of adsorption of n-alkanes and polar probes. Whereas, the other proposed methods do not take into consideration the effect of the temperature on the deformation polarizability or on the topological index.

Analysis of the results

Lanin et al. [41] determined the adsorption properties of titanium dioxide and obtained for TiO_2 surface the acid base constants $K_A=0.18$, $K_D=1.19$ and $K_D/K_A=6.61$. These values are very close to those obtained by the present study when using the topological index method [39]. Lee et al. [42] determined the relative acidity K_A/K_D of non-treated titanium dioxide but the ratio was expressed in mol/kcal, because of the use of the classical method with K_A (unitless) and K_D (kcal/mol). They obtained $K_A/K_D=0.90$ mol/kcal. This value can be converted to unitless ratio by using the following relation [43]:

$$K_A(kcal/mol) = \frac{40(kcal/mol)}{100} K_A(\text{unitless}) \quad (13)$$

Therefore, the unitless ratio K_A/K_D (from the values given by Lee et al. [42] is equal to $K_A/K_D=0.36$ or $K_D/K_A=2.78$. This result approaches the result that we obtained by using the vapor pressure method ($K_D/K_A=3.97$) but it is very different from the last method using the topological index. Bogillo and Voelkel [44] also studied the surface properties of the titanium dioxide with is modified forms. By using the vapor pressure method they obtained $K_A/K_D=-0.138$ mol/kcal and with the polarizability method the ratio was $K_A/K_D=0.464$ mol/kcal. These values can be converted to the following unitless ratios $K_D/K_A=-18.16$ and $K_D/K_A=5.40$. The negative value obtained by Bogillo and Voelkel cannot be admitted and probably they committed a mistake in their calculations. However, the second value obtained by the polarizability method, can be approached to the value obtained by our study.

It can be conclude that the acid-base surface properties of titanium dioxide strongly depend on the chosen methods of the determination of the specific free enthalpy of interaction between the polar molecules and the solid substrate. The method using the vapor pressure of molecules gives the more accurate values of K_A and K_D . However, the various results obtained by the different IGC methods can be only considered as qualitative. In this study, we deduced that the titanium dioxide exhibits more basic than acidic surface.

Conclusion

In this study, we determined the acid base interactions and the surface properties of titanium dioxide catalyst by inverse gas chromatography at infinite dilution. The curves of $\ln V_n=f(1/T)$ allowed to obtain the differential heat, the enthalpy and entropy of adsorption of different organic probes adsorbed on the titanium oxide surface. We separated the two polar and dispersive contributions of polar molecules adsorbed on the Titania surface. For the first time, we gave a linear relation between the polar enthalpy of adsorption of probes and their relative polarities with an excellent accuracy. The different molecular models of the surface areas of n-alkanes were applied to calculate the dispersive component γ_s^d of the surface energy of TiO_2 catalyst. The obtained results clearly showed a linear dependency of γ_s^d against the temperature for all used model of surface area of n-alkanes. The application of Saint-Flour and Papier method allowed determining the specific free energy of adsorption as a function of the temperature and then to deduce the specific enthalpy and entropy of polar probes adsorbed on titania surface. It was proved that titanium dioxide surface is an amphoteric surface with stronger basic

character. The acid K_A and base K_D constant of this catalyst were determined $K_A=2.73$, $K_D=10.82$ and $K_D/K_A=3.97$. The results obtained by zetametry for the dispersion of titania particles in organic liquids allowed to obtain the acceptor ANS' and donor DNS' numbers of the titania catalyst: $DNS'=46$, $ANS'=11$ and $DNS'/ANS'=4.18$. These results proved that $DNS'=4.25 K_D$ and $ANS'=4.03 K_A$ showing an acid base character of TiO_2 catalyst in organic liquid medium obtained in zetametry, larger than that obtained in inverse gas chromatography at infinite dilution. The comparison of the method based on the vapor pressure to those using the deformation polarizability and the topological index led to conclude that all method gave an identical order of the interaction force of the various polar probes and similar acid base constant ratio K_D/K_A . The method using the vapor pressure seems to be the best one, because it is based on the dependency of the vapor pressure of molecules on the temperature and the obtained results by this method are more accurate.

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