PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

The Adsorption Properties of Titanium Dioxide

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Abstract—The adsorption properties of titanium dioxide were studied by gas chromatography. We used organic compounds from different classes, namely, *n*-alkanes, *n*-alkenes (C_6-C_8), and polar compounds (electron donors and acceptors) as test adsorbates. The differential heats of adsorption and the contributions of dispersion and specific intermolecular interaction energies were determined for the systems from the experimental retention data. The electron-donor and electron-acceptor characteristics of the ultimately hydroxylated surface of TiO_2 were evaluated.

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INTRODUCTION

Gas chromatography has been successfully used in studies of the surface chemistry and adsorption properties of various adsorbents at low surface occupancies when adsorbate-adsorbent interactions predominate [1]. In this work, gas chromatography was used to study the adsorption properties and surface chemistry of titanium oxide polycrystals used as catalysts, photocatalysts, pigments, polymers, and adsorbents. Titanium oxide has high hydrolytic, chemical, and mechanical stability [2]. Its surface contains Lewis acid and base centers, which largely determine its adsorption and catalytic properties [2].

EXPERIMENTAL

Titanium oxide (Aldrich, USA) was studied as an adsorbent. Its specific surface (S_{sp}) determined by the thermal desorption of nitrogen was $6.3 \text{ m}^2/\text{g}$. We used *n*-alkenes (C_6-C_8), *n*-alkanes (C_6-C_9), and their derivatives (electron donors and acceptors) as test adsorbates. Their characteristics are listed in Table 1.

Apparatus and Experimental Techniques

Gas chromatographic measurements were conducted on a KristalLyuks-4000M chromatograph with a katharometer as a detector. Glass columns $(200 \times 2 \text{ mm})$, 1.095 g adsorbent sample, and helium as a carrier gas were used. When the chromatographic retention parameters were measured, the carrier gas flow rate was kept constant, ~25 ml/min. Before experiments, the adsorbent was conditioned in a helium flow in a chromatographic column at 150°C for 20 h.

To study adsorption properties, we measured the specific retention volumes for all adsorbates at low

Adsorbate	М	μ, D	α, Å ³	DN	AN	DN/AN
<i>n</i> -C ₆ H ₁₄	86.17	0	11.9	_	_	0
<i>n</i> -C ₇ H ₁₆	100.2	0	13.7	_	_	0
$n-C_8H_{18}$	114.0	0	15.6	_	-	0
CHCl ₃	119.4	1.15	8.23	0	23	0
C ₆ H ₆	78.0	0	10.4	0.42	8.2	0.05
CH ₃ NO ₂	61.0	3.54	7.2	11.3	20.5	0.55
CH ₃ CN	41.1	3.90	5.4	59.0	18.9	3.12
$(CH_3)_2CO$	50.18	2.80	6.6	71.1	12.5	5.69
C_4H_8O	72.10	1.63	7.65	83.6	8.0	10.45
CH ₃ COOC ₂ H ₅	88.1	1.78	9.0	71.5	9.3	7.7

Table 1. Characteristics of test adsorbates

Note: *M* is the molecular weight, μ is the dipole moment, α is the total polarizability of the molecule, and *DN* and *AN* (kJ/mol) are the electron-donor and electron-acceptor energy characteristics of molecules.



Fig. 1. Dependences of $\ln V_g$ on 1/T for the adsorption of alkanes on TiO_2 : (1) n-C₉H₂₀, (2) n-C₈H₁₈, (3) i-C₈H₁₈, (4) n-C₇H₁₆, and (5) n-C₆H₁₄.

occupancies, when adsorbate-adsorbate interactions were yet unnoticeable, and determined the thermodynamic characteristics of adsorption.

The specific retention volumes V_g were calculated by the equation [3]

$$V_g = \frac{t_r F_{\rm msd} T_{\rm col} p_{\rm msd}}{T_{\rm r} p_0 m}$$

where $t_r = t_c - t_0$ (t_r is the corrected adsorbate retention time, s; t_c is the adsorbate retention time, s; and t_0 is the elution time of an unadsorbed substance); *F* is the carrier gas flow rate (cm³/s); $p_{msd} = p_0 - p_{H_2O}$ (p_0 is the pressure at the exit of the column (atmospheric pressure, torr), and p_{H_2O} is the water vapor pressure at room temperature, torr); T_{col} is the thermostat temperature, K; T_r is room temperature, K; *m* is the adsorbent mass, g; and *f* is the coefficient of the column pressure gradient effect on *F*.



Fig. 2. Dependences of $\ln V_g$ on 1/T for the adsorption of polar adsorbates on TiO₂: (1) CH₃NO₂, (2) CH₃CN, (3) CH₃COOC₂H₅, (4) CHCl₃, and (5) (CH₃)₂CO.

The differential molar change in the internal energy of adsorption $(-\Delta U)$, which equals the differential heat of adsorption (Q_v) , was determined from the dependence of $\ln(V_g)$ on inverse temperature 1/T,

$$\ln V_{\varrho} = A + B/T. \tag{1}$$

Here, A and B are the constants given by the equations

$$A = \Delta S/R + 1,$$

$$B = -\Delta U/R = O_{*}/R.$$

1

where ΔS is the standard entropy; ΔU is the differential molar change in internal energy, which equals the differential heat of adsorption Q_{v} ; and R is the gas constant [3].

RESULTS AND DISCUSSION

The temperature dependences of the specific retention volumes $\ln V_g = f(1/T)$ were determined for each adsorbate at low occupancies. The dependences over the temperature range 50–100°C were almost linear (the correlation coefficient was $R \ge 0.99$). Figure 1

Adsorbate	<i>T</i> , °C	-A	В	$-\Delta U$, kJ/mol	$-\Delta S$, J/(mol K)	V_g , cm ³ /g (50°C)
<i>n</i> -C ₆ H ₁₄	50-100	10.443	3730.1	31	86.8	4.7
<i>n</i> -C ₇ H ₁₆	50-100	10.521	4202.7	35	87.5	14.3
<i>n</i> -C ₈ H ₁₈	50-100	10.818	4651.9	39	89.9	40.5
$n - C_9 H_{20}$	50-100	11.59	5250.5	43	96.4	105.6
C ₆ H ₆	50-100	18.061	6394.2	53	150	5.0
CHCl ₃	50-100	16.515	5504.0	46	137.3	2.5
CH ₃ NO ₂	50-100	17.611	6357.2	53	146.4	13.8
CH ₃ CN	50-100	21.344	6213.4	52	177.5	5.6
$(CH_3)_2CO$	50-100	19.333	6026.5	50	160.7	1.5
C ₂ H ₅ COOCH ₃	50-100	19.072	6350.3	53	158.6	3.98
C ₄ H ₈ O	50-120	10.616	5390.2	45	88.3	_

Table 2. Coefficients of (1) and thermodynamic characteristics of adsorption of organic compounds on TiO_2



Fig. 3. Dependences of the heats of adsorption on the number of carbon atoms in a molecule for (1) *n*-alkenes and (2) *n*-alkanes.

shows these dependences for *n*-alkanes, and Fig. 2, for polar adsorbates. Table 2 lists the temperature range, the coefficients of (1), and the Q_v , ΔS , and V_g values at 100°C.

*The Interaction of the Surface of TiO*₂ with n-Alkanes and n-Alkenes

The differential adsorption heats Q_v determined from the dependence of $\ln V_g$ on 1/T for *n*-alkanes and *n*-alkenes are shown in Fig. 3. The dependences of the heats of adsorption on the number of carbon atoms (n_c) in *n*-alkane and *n*-alkene molecules are linear,

$$Q_{\rm v} = 4.2964 n_{\rm C} + 5.0301, \tag{2}$$

$$Q_{\rm v} = 3.5n_{\rm C} + 19.167. \tag{3}$$

n-Alkanes interact with the surface of TiO_2 (and all other adsorbents) only by dispersion and induction interactions caused by the polarization of molecules by hydroxyl group dipoles on the surface of TiO_2 . The reaction energies are proportional to the polarizability

Table 3. Contributions of the dispersion (Q_{disp}) and specific (Q_{sp}) interaction energies of test adsorbates to the total energy (Q_v) of adsorption on TiO₂ kJ/mol

Adsorbate	Q_v	$Q_{ m disp}$	$Q_{ m sp}$	$Q_{\rm sp}/Q_{\rm v},\%$
<i>n</i> -C ₆ H ₁₄	31	31	0	0
<i>n</i> -C ₇ H ₁₆	35	35	0	0
<i>n</i> -C ₈ H ₁₈	39	39	0	0
$n-C_9H_{20}$	43	43	0	0
C ₆ H ₆	53	27.8	25.2	47.6
CHCl ₃	46	23.2	22.8	49.6
CH ₃ NO ₂	53	21	32	60.3
CH ₃ CN	52	17.2	34.8	66.8
(CH ₃) ₂ CO	50	19.8	30.2	60.4
C ₄ H ₈ O	45	22	23	51.1
CH ₃ COOC ₂ H ₅	53	24.8	28.2	53.1



Fig. 4. Dependences of Q_V for *n*-alkanes on polarizability (α , A^3) on TiO₂.

(α) of molecules. *n*-Alkenes are retained on the surface of TiO₂ better than *n*-alkanes with the same number of carbon atoms. This is explained by the specific interactions of the π bonds of *n*-alkene molecules with active centers (hydroxyl groups) on the surface of TiO₂ in addition to dispersion interactions. The difference between the heats of adsorption of *n*-alkenes and *n*alkanes with the same number of carbon atoms characterizes the influence of the specific interactions of the π electron bonds with hydroxyl groups on the surface of TiO₂ (~9 kJ/mol).

The Interaction of the TiO₂ Surface with Polar Molecules

The adsorption of polar adsorbates leads to dispersion and specific intermolecular interactions. The contribution of dispersion interactions (Q_{disp}) to the total energy of adsorption was determined from the dependence of Q_v on polarizability (α) of *n*-alkane molecules. The dependence of Q_{disp} on the total polarizability of *n*-alkane molecules is linear (Fig. 4),

$$Q_{\rm disp} = 2.1606\alpha + 5.3277, \quad R = 0.9999.$$
 (4)

The contribution of specific interactions (Q_{sp}) to the total energy of adsorption of polar adsorbates was determined from the difference between the heats of adsorption of the substance and *n*-alkane with the same polarizability calculated by (4).

The calculated heats of adsorption of the test substances and contributions of dispersion and specific interactions with TiO_2 are presented in Table 3.

As can be seen from Table 3, the contribution of Q_{sp} to Q_v is substantial for all polar adsorbates on TiO₂ $(Q_{sp}/Q_v > 50\%)$.

Irrespective of the type of intermolecular interactions (electrostatic, orientation, coordination interactions with the formation of donor-acceptor complexes, or hydrogen bonding), the energy of specific interactions has the same nature and depends on the electrondonor and electron-acceptor properties of adsorbate



Fig. 5. Determination of the electron-donor (K_D) and electron-acceptor (K_A) characteristics of the TiO₂ surface; (1) CHCl₃, (2) CH₃NO₂, (3) CH₃CN, (4) (CH₃)₂CO, (5) CH₃COOC₂H₅, and (6) C₄H₈O.

molecules and adsorbent surface. This energy is given by the equation [4]

$$Q_{\rm sp} = K_{\rm D}AN + K_{\rm A}DN,\tag{5}$$

where *AN* and *DN* are the electron-acceptor and electron-donor numbers of adsorbate molecules [5] and K_D and K_A are the electron-donor and electron-acceptor characteristics of the adsorbent surface. Equation (5) can be written as

$$Q_{\rm sp}/AN = K_{\rm D} + K_{\rm A}DN/AN, \tag{6}$$

which allows K_D and K_A of TiO₂ to be evaluated.

Figure 5 shows the dependences of Q_{sp}/AN on DN/AN. The K_D and K_A values determined from these dependences are 1.19 and 0.18. It follows that the TiO₂ surface has both electron-donor and electron-acceptor centers. Such centers can be surface hydroxyl groups,

whose concentration on the surface is ~8 groups/nm² [6]. Two types of hydroxyl groups exist on the surface of TiO₂, namely, terminal groups coordinated to one Ti atom and bridging groups coordinated to two Ti atoms [7]. Terminal hydroxyl groups possess basic (electrondonor) properties and can participate in cation exchange; bridging groups have acidic (electron-acceptor) properties. The difference between terminal and bridging groups is confirmed by the spectral and adsorption data [8]. For example, organic amines are primarily (and very actively) adsorbed on bridging hydroxyl groups [9].

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