

## **Inverse gas chromatography of chromia. Part I. Zero surface coverage**

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The surface properties of the solid obtained from colloidal chromia were investigated by inverse gas chromatography (IGC), at zero surface coverage conditions. The solid samples I dried at 423 K and II heated at 1073 K in the amorphous and crystalline form, respectively, were studied in the temperature range 383–423 K. The dispersive components of the surface free energies, enthalpies, entropies, and the acid/base constants for the solids were calculated from the IGC measurements and compared with the data for a commercially available chromia (III). Significantly lower enthalpies and entropies were obtained for cyclohexane on solid II and chloroform, highly polar organic, on solid I. The dispersive contributions to the surface energy of solid II and III were similar, but much greater in the case of solid I. All the sorbents had a basic character, with the  $K_D/K_A$  ratio decreasing in the order I > II > III. The retention and resolution in the separation of a vapour mixture of C<sub>5</sub>–C<sub>8</sub> *n*-alkanes on the three substrates were different. A rapid separation was observed on solid II and an enhanced retention on solid I. Generally, the heated chromia (II) exhibited diminished adsorption capacity, and enhanced homogeneity of the surface.

*Keywords:* inverse gas chromatography, chromia, adsorption, thermodynamics.

### INTRODUCTION

Chromia has frequently been used in chemical engineering and materials science, as well as in the food and pharmaceutical industry. Its surface properties are of great importance for many applications. The geometric and electronic properties of chromia surfaces studied by means of various spectroscopic techniques have been reviewed by Henrich and Cox<sup>1</sup> and by Freund *et al.*<sup>2</sup> For physico-chemical processes taking place at the interface, knowledge about the intermolecular interactions is desirable. Various experimental techniques can be applied to obtain an insight into the properties of chromia as a sorbent in the adsorption from a solution or from the gas phase. In the past few decades, inverse gas chromatography (IGC) as a relatively rapid and simple technique, with good accuracy, low cost and available equipment, has been extensively used as a tool for solid surface characteriza-

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tion. Using IGC at zero coverage (IGC-ZC), the surface properties of various materials such as polymers,<sup>3-7</sup> carbons,<sup>8-12</sup> inorganic salts,<sup>13,14</sup> composites,<sup>15</sup> natural materials<sup>16-19</sup> and so on, were investigated. Although, many inorganic oxides, such as silica,<sup>20-27</sup> alumina,<sup>28-30</sup> zirconia,<sup>30-32</sup> have been studied by IGC-ZC from its early development stage up to nowadays, our literature review revealed no article devoted to chromia.

In the present paper, the thermodynamic functions for the adsorption of various organic compounds on a chromia surface and the acid/base properties of amorphous and crystalline forms of chromia were investigated.

### IGC background

The theory relating IGC data to the surface properties of solids developed years ago is given in detail elsewhere.<sup>33,34</sup>

In IGC at zero surface coverage (IGC-ZC), the thermodynamic functions of adsorption of organic compounds onto an adsorbent, packed into a chromatography column, may be obtained from the adsorbate net retention volume,  $V_N$ ,

$$V_N = jF_f \frac{(p_o - p_w)}{p_o} \frac{T}{T_f} (t_R - t_o) \quad (1)$$

The terms used in the equations are given in the list of symbols. From  $V_N$ , the surface partition coefficient is determined as  $K_s = V_N / (m S_{a/N2})$ . In addition,  $V_N$  is related to the free energy of adsorption by the following equation

$$G_a^\circ = RT \ln \frac{V_N p_{s,g}}{m S_{a,s}} \quad (2)$$

where  $p_{s,g} = 101 \text{ kN/m}^2$  (101 kPa), and  $S_{a,s} = 0.338 \text{ nM/m}$ , taken as the standard reference state.<sup>35</sup>

The well known Van't Hoff equation is used to derive  $H_a^\circ$ , which corresponds to the slope of a  $G_a^\circ/T - 1/T$  straight-line plot.<sup>36</sup> Then, the parameter  $S_a^\circ$  can be calculated using a common relation

$$G_a^\circ = H_a^\circ - T S_a^\circ \quad (3)$$

The function  $G_a^\circ$  can be considered as the sum of energies arising from the dispersive component (from the London and van der Waals forces) and the specific component (from the Lewis acid/base interactions and hydrogen bonding).<sup>37</sup> In the case of *n*-alkane adsorbates, only dispersive forces contribute to  $G_a^\circ$ . The slopes of the linear plots  $G_a^\circ$  versus number of C atoms in *n*-alkanes give  $G_{aCH_2}^\circ$ , which can be used to relate  $G_a^\circ$  to  $S_{a,d}^\circ$ .<sup>38</sup>

$$S_{a,d}^\circ = \frac{G_{aCH_2}^{\circ 2}}{4 N_A^2 a_{CH_2}^2} \quad (4)$$

Brookman and Sawyer<sup>39</sup> described  $G_a^S$ , which corresponds to acid-base surface interactions, as the difference in the ordinates between the point of specific polar adsorbate and a reference *n*-alkane having the same  $T_b$ . Consequently,  $V_N$  data are re-

lated to  $G_a^S$  by the following equation

$$G_a^S = RT \ln \frac{V_N}{V_N^{\text{ref}}} \quad (5)$$

From  $G_a^S$  the temperature function,  $H_a^S$  is derived as stated above.

Following the Saint-Flour and Papirer approach,<sup>40</sup>  $K_D$  and  $K_A$  of the adsorbent may be obtained as the slope and the intercept from the expression

$$-\frac{H_a^S}{AN^*} - \frac{DN}{AN^*} K_A = K_D \quad (6)$$

The  $K_D/K_A$  ratio is a measure of the surface acidity and basicity. Thus, for a ratio  $K_D/K_A > 1$ , the surface is considered to be alkaline, but acidic for  $K_D/K_A < 1$ .

#### EXPERIMENTAL

The colloidal dispersion of chromia used as a precursor was obtained by forced hydrolysis of a chromium chloride solution at an elevated temperature.<sup>41</sup> From this sol, solid oxide residues were prepared by slow coagulation caused by the controlled addition of 0.1 M KOH. The coagulate was extensively washed with reagent grade water, and gradually heating up to 423 K (solid I), or 1073 K (solid II), and kept at the temperatures for an additional 4 h. For comparison, a commercial chromia (III), (Fluka 27085) was used as received.

Elemental analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin-Elmer ICP/6500) and energy dispersive X-ray spectrometry (EDXRF) (Canberra SL30170, Si(Li), <sup>241</sup>Am, <sup>55</sup>Fe, <sup>109</sup>Cd) showed insignificant amounts of impurities in all solids. The X-ray diffraction technique (XRD) (Siemens-D 500, CuK $\alpha$ ) revealed amorphous (I), and crystalline (II and III) solids (Fig. 1). The surface areas measured by IGC at finite coverage condition<sup>42</sup> were 77, 13 and 17 m<sup>2</sup>/g, for solid I, II and III, respectively. The obtained solids were sieved, and the fraction with  $d < 0.1$  mm was used to fill a 0.25 m long (2.2 mm ID) stainless steel chromatographic column. After column conditioning, overnight in a nitrogen flow at 423 K, the IGC experiments were performed.

TABLE I. Acid-base characteristics of IGC adsorbates<sup>43,44</sup>

Adsorbate	$DN$ /(kJ/mol)	$AN^*$ /(kJ/mol)	Lewis characteristics
C <sub>5</sub> -C <sub>8</sub> **	0	0	Neutral
CHCl <sub>3</sub>	0	22.7	Acidic
EtAc	71.1	6.3	Amphoteric
DEE	80.3	5.9	Medium basic
THF	83.7	2.1	Basic

\*\* C<sub>5</sub>-C<sub>8</sub> = *n*-C<sub>5</sub>H<sub>12</sub>, *n*-C<sub>6</sub>H<sub>14</sub>, *n*-C<sub>7</sub>H<sub>16</sub>, *n*-C<sub>8</sub>H<sub>18</sub>, *c*-C<sub>6</sub>H<sub>12</sub>.

The retention data were obtained using a Spectra-Physics model SP7100 gas chromatograph with a flame ionization detector (FID) maintained at 250 °C. The detector operated in its maximum sensitivity mode and Varian Star 4.5 software was employed to collect the data. To ensure flash vaporization of the adsorbate vapour, the injector was set at 220 °C. Purified nitrogen at a flow rate of 3.0 ml/min was used as the carrier gas, while methane, as an unretained compound, was used to determine the dead volume. Appropriate corrections to the pressure drop along the column were made on the basis of the pressure at the injection and outlet ports. The retention times were the average of several injections for each sample and condition. All experiments were performed in the temperature range from 383 to 423 K, at 10 K intervals. To ensure a valid approximation of zero coverage, minimum detectable amounts of adsorbate vapour were injected. Relevant IGC results from the retention data collected were calculated by a program developed for the purpose.

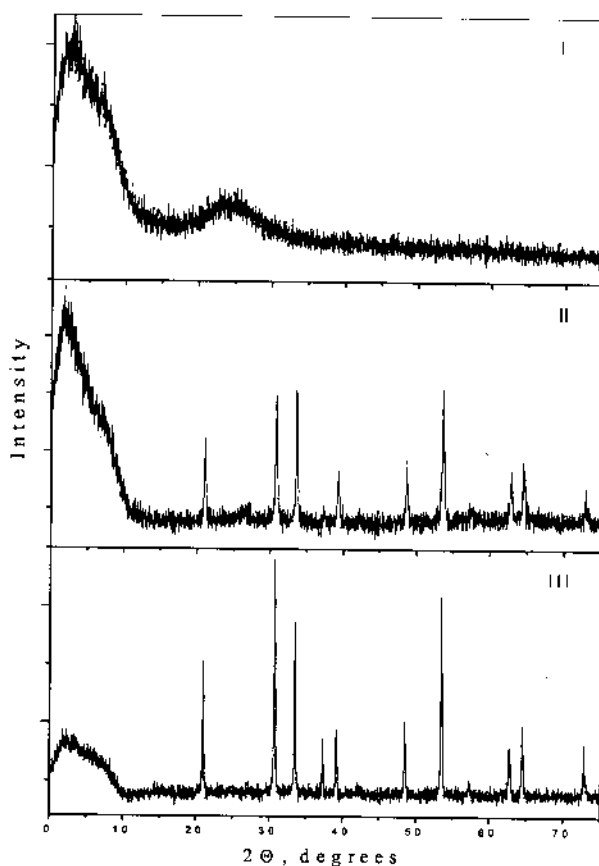


Fig. 1. X-Ray diffraction patterns of chromia samples I, II and III.

The following test compounds, supplied from various commercial sources, were used as IGC adsorbates: *n*-pentane ( $n\text{-C}_5\text{H}_{12}$ ), *n*-hexane ( $n\text{-C}_6\text{H}_{14}$ ), *n*-heptane ( $n\text{-C}_7\text{H}_{16}$ ), *n*-octane ( $n\text{-C}_8\text{H}_{18}$ ), chloroform ( $\text{CHCl}_3$ ), di-ethyl ether (DEE), ethyl acetate (EtAc), tetrahydrofuran (THF), cyclohexane ( $c\text{-C}_6\text{H}_{12}$ ), benzene, and toluene. They were of HPLC grade and used as received. The acid-base constants relevant to IGC for several adsorbates are listed in Table I.<sup>43,44</sup>

#### RESULTS AND DISCUSSION

The sorption properties of the solids in both the amorphous and crystalline form were investigated at zero surface coverage condition (Henry's law region) where lateral interactions between the molecules adsorbed at the surface can be neglected. Well-defined Gaussian peaks with the same retention volumes for repeated injections of various small quantities of adsorbate vapour indicate that the measurements were performed at the linear part of the adsorption isotherms.

Table II presents the surface partition coefficients,  $K_s$ , of selected adsorbates on the studied solids at two temperatures.

TABLE II. Surface partition coefficients,  $K_s(\text{cm}^3 \text{m}^{-2})$ , of selected adsorbates on (I, II, III) chromia

Adsorbate	$T/\text{K}$	$K_s/\text{cm}^3\text{m}^{-2}$		
		I	II	III
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	423	0.109	0.070	0.037
	403	0.164	0.097	0.052
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	423	0.307	0.141	0.080
	403	0.504	0.217	0.136
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	423	0.807	0.314	0.171
	403	1.514	0.511	0.309
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	423	2.172	0.760	0.383
	403	4.475	1.362	0.755
CHCl <sub>3</sub>	423	0.053	0.233	0.051
	403	0.065	0.460	0.090
EtAc	423	–	2.788	0.233
	403	–	5.580	0.719
DEE	423	0.107	0.346	0.172
	403	0.195	0.741	0.438
THF	423	0.391	1.704	0.186
	403	0.589	2.917	0.373
<i>c</i> -C <sub>6</sub> H <sub>12</sub>	423	0.042	0.060	0.012
	403	0.070	0.083	0.023
Benzene	423	0.176	0.182	0.080
	403	0.348	0.338	0.146
Toluene	423	0.521	0.412	0.207
	403	1.198	0.823	0.440

Remarkably higher  $K_s$  values for *n*-alkanes on solid I were obtained. These values were alternatively different for the other adsorbates on solids I and II. However, solid III exhibits distinctly smaller partition. In gas-solid partition chromatography (GSC), lower  $K_s$  values for *c*-C<sub>6</sub>H<sub>12</sub> than for the corresponding *n*-alkane (*n*-C<sub>6</sub>H<sub>14</sub>) are commonly observed. For geometric reasons, the six C-atoms can simultaneously approach the plane in the case of *n*-C<sub>6</sub>H<sub>14</sub>, whereas only three or four can in the case of *c*-C<sub>6</sub>H<sub>12</sub>. This is considered to be the consequence of the existence of both the “boat” and “chair” isomers of cyclohexane and the steric effect on adsorption.<sup>20</sup> However, in gas-liquid partition chromatography (GLC), *c*-C<sub>6</sub>H<sub>12</sub> is retained more strongly than *n*-C<sub>6</sub>H<sub>14</sub>.<sup>3</sup>

The difference in  $K_s$  values between benzene and *n*-C<sub>6</sub>H<sub>14</sub> results from the interactions occurring between the  $\pi$ -electrons in the aromatic rings and the surface hydroxyl groups, similar to hydrogen bonding. However, toluene interacts more intensively with all solids than benzene due to the additional CH<sub>3</sub>-group in its molecule. The  $K_s$  for this extra methyl group differs substantially from one solid to another (I, II and

III), and is much higher than that for the *n*-alkane with the difference in one C-number, which means that the branching in the toluene molecule has no effect on the sorption.

#### Enthalpy and entropy of adsorption

The thermodynamic functions for the adsorption of the studied organics at zero surface coverage conditions are presented in Table III.

It is evident from Table III that stronger interactions (higher  $-H_a^\circ$ ) occur with the adsorbates having higher C-numbers, except in the cases where specific interactions prevail. Only for solid II are the  $H_a^\circ$  and  $S_a^\circ$  values for *c*-C<sub>6</sub>H<sub>12</sub> lower than for *n*-C<sub>6</sub>H<sub>14</sub>. Returning to the retention times data, the average  $t_R$  ratios between *n*-C<sub>6</sub>H<sub>14</sub> and *c*-C<sub>6</sub>H<sub>12</sub> are 2.1 (solid II), 1.8 (solid I), and 2.6 (solid III). However, the high temperature gradient for the retention results in high numerical values of these functions for solid I and, particularly, for solid III.

TABLE III. Standard adsorption enthalpy,  $H_a^\circ$ , and entropy,  $S_a^\circ$ , of selected adsorbates on (I, II, III) chromia in the temperature range 383–423 K

Adsorbate	$-H_a^\circ$ (kJ/mol)			$-S_a^\circ$ (J/mol K)			$-S_a^\circ$ (J/mol K)				
	I	II	III	I	II	III					
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	28.91	26.13	23.78	39.4	0.1	36.5	0.1	35.9	0.2	52.4	0.2
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	33.04	33.58	31.94	40.5	0.4	48.5	0.2	48.8	0.2	53.5	0.4
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	47.11	40.99	37.06	66.3	0.2	59.4	0.3	54.6	0.3	54.2	0.9
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	49.29	44.67	45.49	62.5	0.2	60.6	0.2	67.5	0.2	54.3	0.2
CHCl <sub>3</sub>	18.62	42.58	43.07	21.3	0.3	64.7	0.4	79.7	0.4	54.5	0.2
EtAc	–	50.72	51.91	–	–	64.5	0.3	85.5	1.2	53.3	0.1
DEE	40.41	49.54	34.31	66.7	0.2	78.6	0.2	46.6	1.4	52.5	0.2
THF	32.82	47.93	49.25	38.1	0.4	62.2	0.4	89.9	0.1	52.4	0.2
<i>c</i> -C <sub>6</sub> H <sub>12</sub>	35.49	22.06	40.84	62.7	0.1	28.2	0.1	85.4	0.5	53.0	0.2
Benzene	42.19	44.17	40.17	66.5	0.2	71.2	0.1	68.5	0.2	52.7	0.2
Toluene	56.93	48.83	53.59	92.3	0.5	75.4	0.1	92.4	0.3	53.4	0.2

The theoretical entropy changes for the adsorption of the investigated adsorbates was calculated according to de Boer<sup>35</sup> as the difference in the entropy of the adsorbate as an ideal gas in three-dimensional translation movement,  $3S_t - 3S_t = R \ln(M^{3/2}T^{5/2}) - 9.62$ , and the entropy of an ideal two-dimensional gas adsorbed at the surface having unrestricted freedom of movement in two directions only but not in the direction perpendicular to the surface,  $2S_t - 2S_t = R \ln(MT A_s) + 275.31$ . For most adsorbates, the values between  $S_a^\circ$  (  $S_a^\circ = 2S_t - 3S_t$  ) and  $S_a^\circ$  are different. These discrepancies result from polar and specific interactions occurring between the adsorbate molecule and the surface functional groups, which cause an additional restriction in the rotational and vibrational freedom of the adsorbate. All  $-S_a^\circ$  values fall within a narrow range from 52 to 55 J/mol K, however,  $-S_a^\circ$  values appear within a wider range from 35 to 93 J/mol K.

According to the obtained data, the adsorption process is less intense on crystalline than on amorphous chromia, except for the adsorbates with high proton acceptor-donor ability ( $\text{CHCl}_3$ , DEE, THF).

It should be mentioned that under the given conditions, EtAc could not be eluted on solid I even for several hundreds minutes. At this stage, it is not possible to say exactly what type of interactions between sorbent I and EtAc occur, but this strong affinity indicates the possible formation of acetate-chromium chemical bonding.

#### Dispersive component of the surface free energy

The dispersive surface energy of chromia,  $\gamma_s^d$ , is an important parameter of the sorption process taking place at the surface, *i.e.*, the ability of the surface to establish non-polar intermolecular interactions. The  $\gamma_s^d$  values were calculated (using Eq. (4)), from the incremental free energies,  $G_a^\circ \text{CH}_2$ , obtained from Fig. 2 as the slopes of  $-G_a^\circ$  vs.  $n_C$ . The  $-G_a^\circ \text{CH}_2$  values increase with increasing  $n_C$ , and decreasing temperature. Solid I, which was not heated, has a much greater incremental  $G_a^\circ \text{CH}_2$ -values than the solids II and III. This is in accordance with the loss of surface heterogeneity caused by thermal treatment. The  $\gamma_s^d$ -values obtained from IGC for the studied chromias at different temperatures are shown in Table IV. The  $\gamma_s^d$  values are much higher when solid I was used as the adsorbent, implying strong non-specific adsorption.

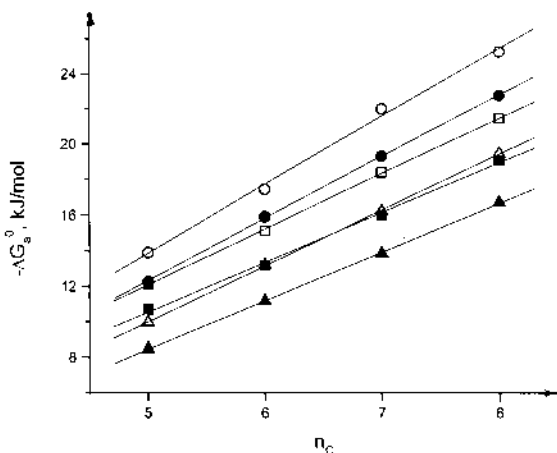


Fig. 2. Plots of  $-G_a^\circ$  versus carbon number of *n*-alkanes for chromia samples (I—●,○; II—■,□; III—▲, ) at 423 K (filled symbols) and 383 K (open symbols).

TABLE IV. Dispersive component of the surface free energy for (I, II, III) chromia

T/K	$\gamma_s^d/\text{mJ m}^{-2}$		
	I	II	III
423	83.46	53.56	51.11
413	86.29	54.57	54.57
403	89.20	56.79	57.70
393	92.71	59.02	59.68
383	94.42	61.67	62.48

For all three sorbents (I, II, III), the  $s^d$  values gradually decrease with temperature, according to the relationships:  $s^d(\text{I}) = 203.4 - 0.283 T$ ,  $s^d(\text{II}) = 140.4 - 0.206 T$ , and  $s^d(\text{III}) = 169.3 - 0.278 T$ . The surface free energy appears to be related to the distribution of surface oxygen-containing functional groups, the desorption of which from solid II is significantly reduced  $s^d(\text{II})$ , compared to from solid I,  $s^d(\text{I})$ .

#### Acid/base interactions

The role of the specific part of the interactions may be evaluated from  $G_a^S$ , which corresponds to the difference between the standard free energy of adsorption of a polar adsorbate and the corresponding value for a hypothetical *n*-alkane, of the same  $T_b$ . According to this approach, Fig. 3 can be used to elucidate the extent of specific processes at the surface from the vertical distance between the *n*-alkane line and the polar adsorbate point. For the sake of clarity,  $-G_a^S$  vs.  $T_b$  plots for only one column temperature are presented.

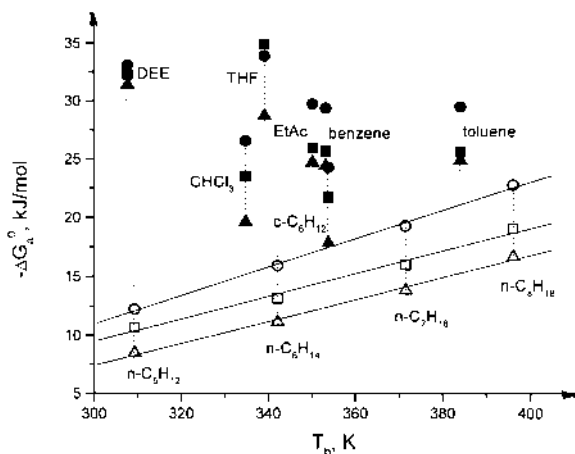


Fig. 3. Plots of  $-G_a^S$  versus  $T_b$  for chromia samples (I—●, ○; II—■, □; III—▲, ) at 423 K.

The  $G_a^S$  values for the polar probes located as a consequence of their specific interaction with both the strong base (THF) and the strong acid ( $\text{CHCl}_3$ ) above the linear ( $n\text{-C}_5\text{H}_{12} - n\text{-C}_8\text{H}_{18}$ ) plots indicate that the surfaces exhibit both donor and acceptor character.

The specific enthalpy interaction parameter,  $H_a^S$ , for acidic and basic adsorbates was obtained from the linear plot of  $G_a^S/T - 1/T$ , while  $G_a^S$  was calculated from Eq. (5). Equation (6) was then used to calculate the  $K_D$  and  $K_A$  values for each adsorbent as the slopes and the intercepts of the plots given in Fig. 4. The terms,  $DN$  and  $AN^*$ , denote the Gutmann electron-donor and electron-acceptor numbers of the adsorbates.<sup>43</sup> It is noteworthy that the originally proposed  $AN$  term is a unitless parameter, expressed in % or ppm, while the  $DN$  term is in kJ/mol. Riddle and Fowkes have proposed corrections for the adsorbate-surface interactions to convert the  $AN$  values to energy values (kJ/mol),<sup>44</sup> so that the  $K_D/K_A$  ratio could be obtained as a dimensionless parameter. This point is discussed elsewhere.<sup>45</sup> Figure 4 shows the dependencies of



$H_a^S/AN^*$  on  $DN/AN^*$ , plotted for the chromia samples I, II and III. Calculated  $K_D$  and  $K_A$  constants are presented in Table V.

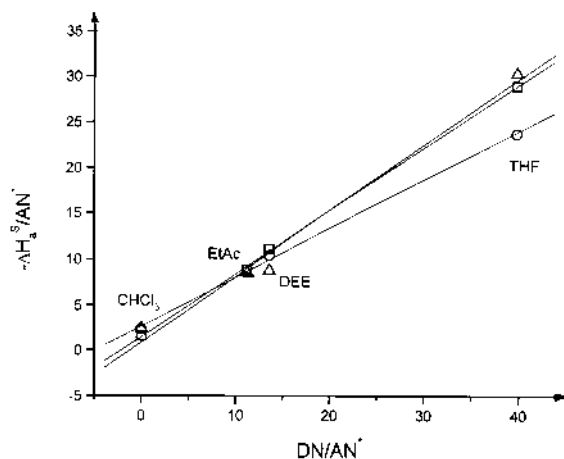


Fig. 4. Plots of  $-H_a^S/AN^*$  versus  $DN/AN^*$  for chromia samples (I—O; II—□; III— ) at 423 K.

TABLE V. Acid/base constants for (I) amorphous and (II, III) crystalline chromia

Chromia	$K_D$	$K_A$	$K_D/K_A$
I	2.65	0.53	4.99
II	1.47	0.69	2.13
III	0.87	0.72	1.21

The overall acid/base character is evaluated from the  $K_D/K_A$  ratio. The resulting  $K_D/K_A$  values for the studied solids imply that solid I has, as expected, a more pronounced basic character. The value being more than twice as high as that found for solid II. Hydroxyl groups act as Lewis centers on the surface, therefore, the greater acidity of the heated solids is attributed to a loss in the number of these groups due to the thermal desorption process.

#### Chromatography of vapour mixture on chromia

For chromatographic separation of a vapour mixture the sorption should be strong enough to ensure that the analyte concentration at the gas-solid interface is almost zero, but not excessively strong to prevent desorption under reasonable conditions, *i.e.*, temperature and time. The use of chromium(III) in the oxide form for hydrogen isotopes<sup>46</sup> and nitrogen-oxygen separation,<sup>47</sup> and in polymeric form for low-molecular size organics,<sup>48</sup> and also as a support for commercial liquid phase packing,<sup>49</sup> revealed its applicability as an inexpensive alternative column packing for some cases of analytical gas chromatography (GC). As an illustration, the GC separation of a C<sub>5</sub>–C<sub>8</sub> *n*-alkane vapour mixture on chromia as the stationary phase is presented in Fig. 5.

The retention and resolution of the separation of the C<sub>5</sub>–C<sub>8</sub> *n*-alkane vapour mixture on the three solids are different. It should be emphasized that the *x*-axis scales in Fig. 5 differ being zero to 90, 12 and 30 min, for the solid I, II and III, respectively. Even

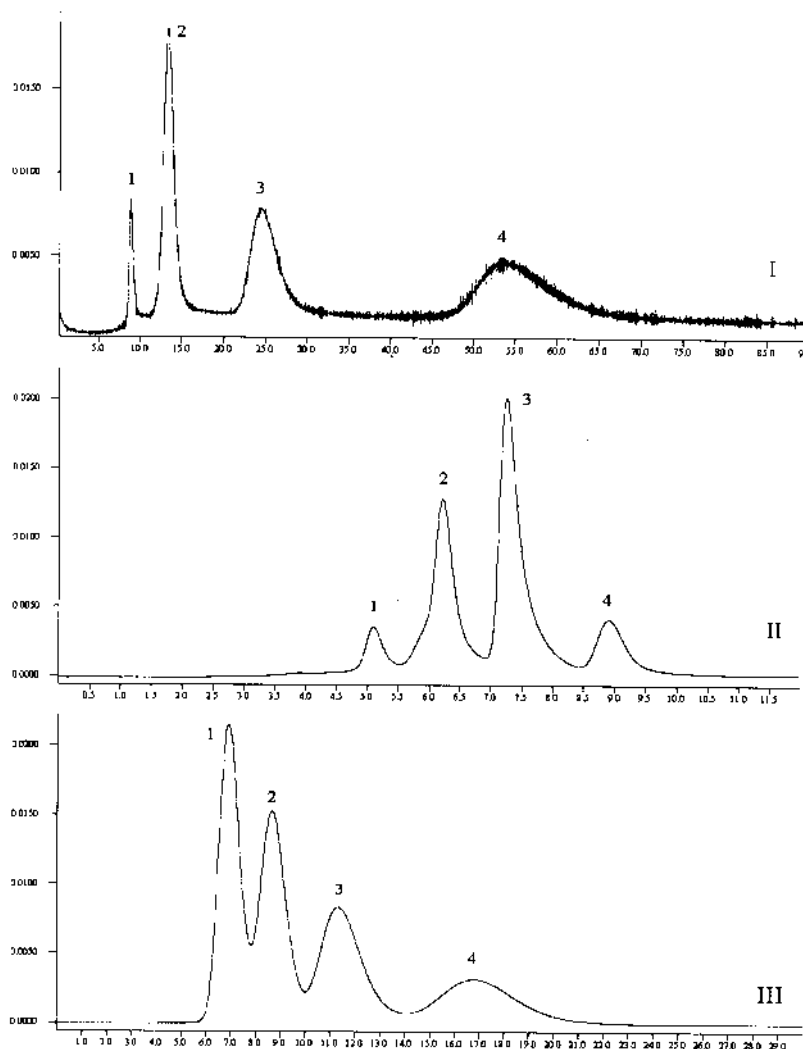


Fig. 5. Chromatograms of an *n*-alkane vapour mixture. Chromia: I, II, III. Temperature program: 50 °C (2 min) ramp 10 °C/min to 150 °C (hold). Peaks: 1)  $n\text{-C}_5\text{H}_{12}$ , 2)  $n\text{-C}_6\text{H}_{14}$ , 3)  $n\text{-C}_7\text{H}_{16}$ , 4)  $n\text{-C}_8\text{H}_{18}$ .

on solid III, the separation is quite satisfactory, when a temperature programmed heating of the column was applied. The peaks are generally narrower when using solid II, with a rapid separation in less than ten minutes. However, the retention is long on solid I. From a parallel IGC study at finite coverage conditions,<sup>42</sup> the numerical values for the adsorption energy distribution function for these solids were obtained. Taking into account those considerations and the chromatograms given in Fig. 5, it can be concluded that heating the solid obtained from a colloidal chromia dispersion produces enhanced homogeneity, but the adsorption ability of its surface, is greatly diminished.

## CONCLUSIONS

Heating the solid phase obtained from a colloidal chromia dispersion causes a change in the structure of the solid and, consequently, a change in its sorption affinity toward organics. The heated chromia exhibits a diminished adsorption capacity for most adsorbates, but an enhanced homogeneity of the surface, which is of great interest in analytical gas chromatography. The dispersive contributions to the surface energy, as a measure of the ability of the chromia surface to establish non-polar intermolecular interactions, are similar for samples II and III (solid of the same crystallinity), but more pronounced for the sample I (amorphous solid). The calculated  $K_D/K_A$  values indicate that chromia has a predominantly basic character. Good resolution of a C<sub>5</sub>–C<sub>8</sub> *n*-alkane vapour mixture was obtained on all solids, a rapid separation in less than ten minutes on sample II, and a long retention on sample I.

## LIST OF SYMBOLS

- $a_{\text{CH}_2}$  – area of an adsorbed methylene group ( $a_{\text{CH}_2} = 0.06 \text{ nm}^2$ )  
 $AN^*$  – Gutmann electron-acceptor number of the adsorbate ( $\text{J mol}^{-1}$ )  
 $DN$  – Gutmann electron-donor number of the adsorbate ( $\text{J mol}^{-1}$ )  
 $F_f$  – carrier gas flow rate ( $\text{m}^3\text{s}^{-1}$ )  
 $j$  – James-Martin gas compressibility correction factor  
 $K_A$  – acceptor parameter  
 $K_D$  – donor parameter  
 $K_s$  – surface partition coefficient ( $\text{cm}^3\text{m}^{-2}$ )  
 $m$  – mass of sorbent in the column (kg)  
 $N$  – Avogadro constant ( $\text{mol}^{-1}$ )  
 $n_C$  – carbon number  
 $p_0$  – column outlet pressure (Pa)  
 $p_{s,g}$  – adsorbate standard state vapour pressure (Pa)  
 $p_w$  – vapour pressure of water at  $T_f$  (Pa)  
 $R$  – gas constant ( $R = 8.3144 \text{ mol}^{-1}\text{K}^{-1}$ )  
 $S_a$  – specific surface area of sorbent ( $\text{m}^2\text{kg}^{-1}$ )  
 $T$  – column temperature (K)  
 $T_b$  – boiling point (K)  
 $T_f$  – ambient temperature (K)  
 $t_0$  – retention time of an unretained compound (methane)  
 $t_R$  – adsorbate retention time (s)  
 $V_N$  – adsorbate net retention volume ( $\text{m}^3$ )  
 $V_N^{\text{ref}}$  – specific retention volume of a corresponding reference *n*-alkane (having the same  $T_b$ ) ( $\text{m}^3$ )  
 $s^d$  – dispersive component of the surface energy ( $\text{mJ m}^{-2}$ )  
 $\text{CH}_2$  – surface energy of a methylene group,  $\text{CH}_2 = 36.8 - 0.058 T (\text{°C})$  ( $\text{mJ m}^{-2}$ )  
 $s$  – two-dimensional standard-state (surface) spreading pressure of the adsorbed gas ( $\text{mN m}^{-1}$ )  
 $G_a^\circ$  – free energy of adsorption ( $\text{J mol}^{-1}$ )

- $G_a^\circ$  CH<sub>2</sub> – free energy of an incremental methylene group (J mol<sup>-1</sup>)  
 $G_a^S$  – specific component of the standard free energy change of adsorption (J mol<sup>-1</sup>)  
 $S_a^\circ$  – standard entropy change of adsorption (J mol<sup>-1</sup>K<sup>-1</sup>)  
 $H_a^\circ$  – standard enthalpy change of adsorption (J mol<sup>-1</sup>)  
 $S_t$  – theoretical entropy changes for adsorption (J mol<sup>-1</sup>K<sup>-1</sup>)  
 ${}_3S_t$  – adsorbate entropy as a ideal three-dimensional gas (J mol<sup>-1</sup>K<sup>-1</sup>)  
 ${}_2S_t$  – entropy of an ideal two-dimensional adsorbed gas (J mol<sup>-1</sup>K<sup>-1</sup>)  
 $A_s$  – area in the standard state for a molecule,  $A_s = 4.08 T \cdot 10^{-16}$  (cm<sup>2</sup>).

## ИЗВОД

## ИНВЕРЗНА ГАСНА ХРОМАТОГРАФИЈА ХРОМОКСИДА. ДЕО I. НУЛТА ПОВРШИНСКА ПОКРИВЕНОСТ

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Испитивана су површинска својства чврсте фазе колоидног хром(III)-оксида методом инверзне гасне хроматографије (IGC) при нултој прекривености. Чврста фаза сола сушена на 423 К (узорак I) у аморфној, и жарена на 1073 К (узорак II) у кристалној форми, је испитивана у температурном опсегу 383–423 К. Из IGC мерења израчунате су вредности дисперзивне компоненте површинске слободне енергије, енталпије, ентропије и кисело/базних константи, за узорке I и II и упоређене са вредностима за комерцијални узорак хром(III)-оксида (III). Значајно мање енталпије и ентропије су добијене за циклохексан на II, и за веома поларну супстанцу, хлороформ, на I. Допринос дисперзивне компоненте површинске енергије је сличан за II и III, а доста је већи за I. Површине сва три сорбента показују базни карактер са смањењем  $K_D/K_A$  односа у смеру I > II > III. Ретенција и резолуција код раздвајања смеше C<sub>5</sub>–C<sub>8</sub> *n*-алкана су различите, са брзом сепарацијом на II, и појачаним задржавањем на I. Жарени узорак је показао смањени адсорпциони капацитет и има хомогенију површину.

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