Gas-Solid Chromatographic Studies of Organic Compounds on Zirconium Oxide Beads[†]

Nebojša M. Djordjević,[††] Slobodan K. Milonjić, and Miroslav M. Kopečni*
Chemical Dynamics Laboratory, The Boris Kidric Institute of Nuclear Sciences,
P.O. Box 522, 11001 Beograd, Yugoslavia
[††]*Chemical Industry "Petrohemija" LTCP, 26000 Pančevo, Yugoslavia*

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Adsorption properties of synthetic zirconium oxide beads were investigated by the gas-solid chromatography (GSC) method. Retentions of numerous alkanes, alkenes, aromatics and chlorinated compounds were measured in a wide temperature region. It appears that the surface activity of an adsorbent can be easily changed by thermal treatment, and in connection with it, the role of crystallographic structure of the adsorbent is emphasized. Thermodynamic parameters obtained were used for explanation of the adsorbent-adsorbate interaction.

The role of GSC in chromatographic practice is twofold: its early application was mainly connected to the analytical problems, while recently there is an increasing interest in physicochemical applications of GSC, among them, special attention is devoted to the adsorption phenomena. GSC measurements offer numerous advantages, the most important are: speed, accuracy, wide temperature region, zero coverage of a surface and above all, this technique provides results in the dynamic conditions.

Apart from silica and alumina, which are extensively used both for practical and physicochemical purposes and therefore are well examined,[1–3] a very few data concerning other metal oxides are available in literature.[4–9] Analytical inapplicability of uncommon metal oxides, due to their surface inhomogeneity and polarity, makes that little attention is paid to those adsorbents. To overcome serious problems linked with surface inhomogeneity and polarity, modifications with various polymeric stationary phases are generally applied.

The first paper dealing with GSC properties of zirconium oxide,[4] thermally pretreated at 1173 K, appeared at the time when the present study was undertaken. Since zirconium oxide may appear in amorphous as well as in monoclinic and tetragonal crystal form, it is normally expected that each modification exhibits different adsorptive properties. There is no information on crystal form used by Lapteva and coworkers,[4] but thermal treatment applied strongly suggests the monoclinic structure. The authors[4] have used three alkanes, *n*-pentane to *n*-heptane, adsorption and thermodynamic data of which were evaluated for temperature region between 493 and 543 K.

Despite the lack of GSC data, zirconium oxide is widely used as an inorganic adsorbent both for anions and cations. It seems that this material deserves more detailed investigations as far as the organic molecule adsorption processes are concerned.

Experimental

The experiments were performed with zirconium oxide precipitated from aqueous zirconium dichloride oxide ($ZrOCl_2 \cdot 8H_2O$) solution with ammonia.[10]

The following procedure was adopted: 30 g of zirconium dichloride oxide was dissolved in 500 ml of 4 mol dm^{-3} of nitric acid, diluted by equal volume of deionized water, and precipitated by 1000 ml of 5% ammonia with vigorous stirring at room temperature. The resultant precipitates were filtrated, thoroughly washed with 1% ammonia solution till the negative reaction of chloride ion, then with deionized water till the neutral reaction. After that, the precipitants were dried in air at 383 K for the period of 10 d. This material was ground and sieved. The fraction of 45—60 mesh was splitted into three portions and each was thermally treated for 4,5 h in air, at 523, 873, and 1173 K, respectively. These materials were used then in GSC experiments as a column packing.

All the chemical used were of analytical grade.

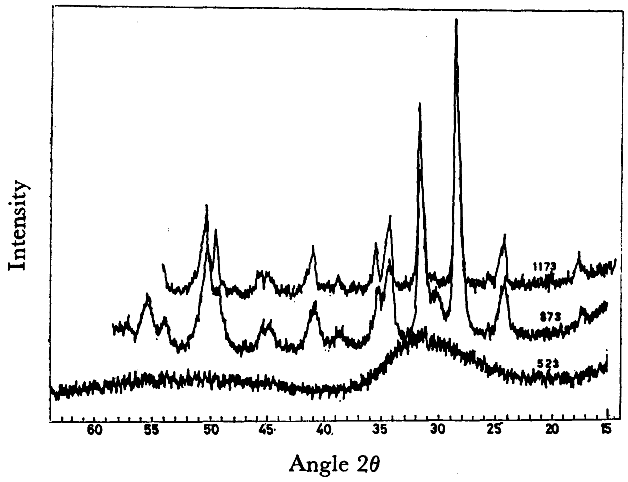

Fig. 1. X-Ray diffraction diagrams for zirconium oxide heated at various temperatures. The figures on the curves represent the heating temperatures, K.

The specific surface areas of the above materials were determined by a Ströhlein area meter using the single point nitrogen adsorption method. The values obtained were 220, 34, and 13 $m^2 g^{-1}$ for materials heated at 573, 873, and 1173 K, respectively. To determine the crystalinity of the packing used, X-ray diffraction patterns were recorded using a Siemens Kristalloflex 4 with a GM counter. The diffractograms obtained are shown in Fig. 1. Diffraction diagram for the material treated at 523 K shows a typical pattern of the amorphous species. The product heated at 873 K is mainly monoclinic with a metastable tetragonal phase indicated

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with a small peak at 30 degrees of 2θ while that one at 1173 K shows the stable monoclinic phase only. These results are in agreement with the recent information published by Sato *et al.*[11)]

All the organic compounds, obtained from various commercial sources, were of analytical reagent grade and used "as received."

A Perkin-Elmer model F 17 and 881 gas-chromatographs were used in the experiments. As a carrier, dry nitrogen was employed, and its flow, depending on the experimental conditions applied, varied in the range of 10 to 20 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, as measured by a soap-bubble flowmeter. The adsorbates were injected as small vapour samples and the retention times were measured by a stop-watch. In all cases, stainless steel columns were used. Prior to the experiments, the packed column was conditioned overnight in a stream of nitrogen at 503 K.

The retention volumes for each adsorbate were measured at 413, 433, 453, 473, and 493 K, with the exception of adsorbates with retention times exceeding 90 min. An average retention from a multiple injection was for the following calculations, and the gas hold up time was assumed to be equal to the retention time of methane at the same temperature. No sample size and tailing effects were observed, except for aromatics at lower experimental temperatures, and such data were omitted from the calculations since they cannot be used for derivation of the thermodynamic data. Generally, sample size effect or tailing indicates inhomogeneity of the adsorbent surface, nonlinearity of the adsorption isotherm or multilayer adsorption.

The net retention volume, V_N, was calculated for each adsorbate from the usual relation,

$$V_\mathrm{N} = j\, t'_\mathrm{R}\, F_\mathrm{C}, \tag{1}$$

where t'_R is the adjusted retention time, F_C is the corrected carrier flow rate and j denotes the James-Martin pressure correction term. The net retention volumes were then converted into the adsorbate distribution coefficients, K_D, at a given temperature, deviding V_N by the total surface area of the adsorbent in the column. The values obtained correspond to the initial slope of the adsorption isotherm. The variation of K_D from one adsorbent to another for the same adsorbate was used then to quantify the changes in the properties of the adsorbents. The isosteric heat of adsorbtion, ΔH, was calculated by plotting ln (K_D/T) *vs.* $(1/T)$, where the linear least-square slopes of the plots were taken to be equal to $-\Delta H/R$ (assuming that ΔH is invariant over the temperature range examined here). The Gibbs free energies of adsorbtion, ΔG, were calculated from the relation $\Delta G = -RT \ln K_\mathrm{D}$, where R is the gas constant. The corresponding entropies of adsorption, ΔS, were calculated from $\Delta S = (\Delta H - \Delta G/T)$.

Results and Discussion

As expected, the distribution coefficients of the adsorbates within the homologous series increase with the increasing chain length as well as with the increasing molecular weights or boiling points, the later dependence is shown in Fig. 2. The straight line connecting experimental points for benzene and its derivates is considerably above the paraffin line because of the specific interactions of adsorbent with the aromatic ring. If we assume that normal alkanes can interact with the surfacenons pecifically only, then the plots similar to Fig. 2 can be used to elucidate the nature of the specific adsorption process. Using this approach, the vertical distance between the normal alkane line (open circles) and any point on the plot for the aromatic line (filled circles) is related to the degree of specific interaction, shown by the compound representing that point.[12)] The plots similar to those in Fig. 2 and conclusions that follow can be drawn for other thermal modifications of the zirconium oxide.

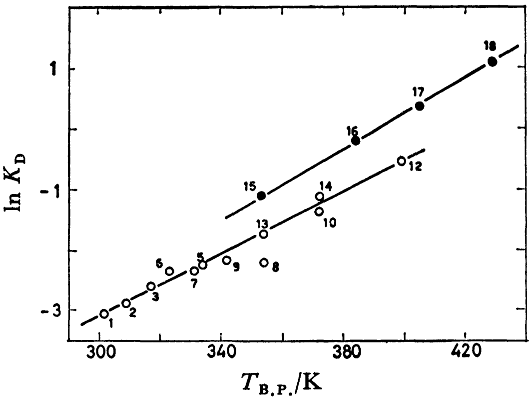

Fig. 2. Logarithm of distribution coefficient at 473 K *vs.* boiling point for zirconium oxide treated at 873 K. 1: 2-Methylbutane, 2: pentane, 3: cyclopentene, 5: 2-methylpentane, 6: 2,2-dimethylbutane, 7: 2,3-dimethylbutane, 8: cyclohexane, 9: hexane, 10: heptane, 12: Octane, 13: 2,4-dimethylpentane, 14: 2,2,4-trimethylpentane, 15: benzene, 16: toluene, 17: chlorobenzene, 18: bromobenzene.

The role of a dominant element in GSC-geometrical factors, is evaluated by comparing the data for hexane and cyclohexane. Although cyclohexane boils 12 K higher than hexane, its retentions are shorter, regardless the thermal treatment of the column material. Due to the shorter retention, the point corresponding to cyclohexane (Fig. 2) lies considerably lower than the saturated hydrocarbon line. Explanation for such a behaviour can be easily found in geometric properties of the molecules under consideration. In the case of hexane, all the six carbon atoms can approach a plane, while for cyclohexane only three or four of them can interact with a surface at the same time, depending on the steric form that cyclohexane may take. Similarlly, the branched saturated hydrocarbons possess less carbon atoms available to contact and therefore to interact with the surface in comparison to the linear molecule with the same carbon atom number. Accordingly, all the branched hydrocarbons are eluted prior to the corresponding linear homologues.

Halogenated compounds interact with zirconium oxide to a great extent, due to their possibility to form stable zirconium dichloride oxide organic complexes.[13)] We believe that this mechanism is responsible for permanent linking of chloroform, dichloromethane and carbon tetrachloride to the column material, even at higher experimental temperatures applied here. On the contrary, halogenated alkenes as well as 1,2-dichlorethane and halogenated benzene derivates are eluted from the column with quite reasonable retentions, in spite of the fact that some of these adsorbates have two possibilities to interact specifically with zirconium oxide, *e. g.* double bond and chlorine atom. Here, the

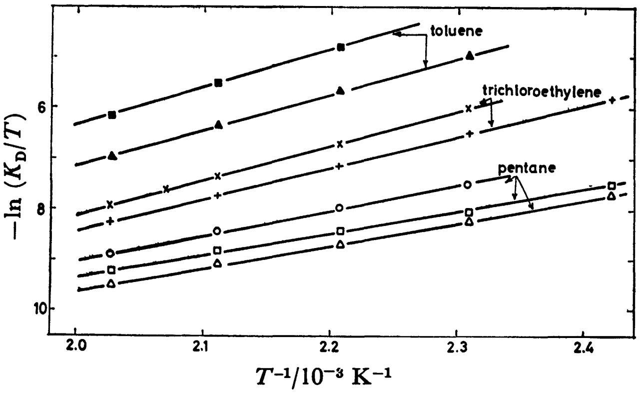

Fig. 3. Representive plots of $\ln(K_D/T)$ *vs.* $(1/T)$ for indicated adsorbates ○, ×, ● ZrO_2 heated at 523 K, △, +, ▲ heated at 873 K and □, ×, ■ heated at 1173 K.

geometric factor is obviously responsible for such a behaviour, a nature of which requires a more detailed examination.

Typical plots of the functionality, $\ln K_D = f(1/T)$ for pentane, trichlorethylene, and toluene are shown in Fig. 3. For other adsorbates studied, similar linear relationships were obtained. The ΔH values calculated from these plots and the corresponding entropies of adsorption are collected in Table 1.

The isosteric heat of adsorption for pentane, hexane and heptane reported by Lapteva and coworkers[4] are −28.9, −34.4, and −41.9 kJ mol^{-1}, respectively. These values are lower than those we found. The different temperature region used in determining the ΔH values can easily produce discrepancy between the values of the isosteric heats. In addition, the mode of preparation of the initial zirconium oxide material, may also contribute to the disagreement in ΔH values.

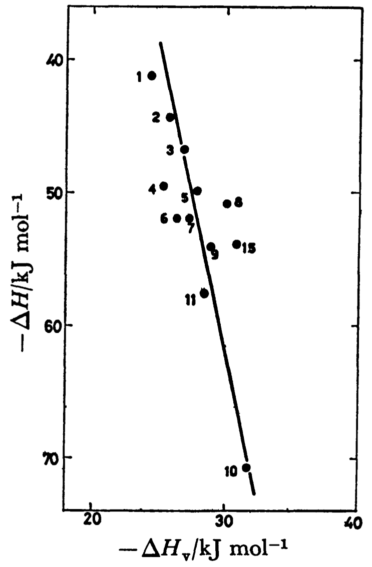

Fig. 4. Dependence of isosteric heat of adsorption on the corresponding heat of vaporization for ZrO_2 thermally treated at 523 K.
Symbols as in Fig. 2. 4: 1-Pentene, 11: 1-hexene.

Dependence of the isosteric heat of adsorption on the heat of vaporization, ΔH_v, are illustrated in Fig. 4, for zirconium oxide treated at 523 K. All the compounds lying on the common straight line represent the same interaction mechanism with the surface. The compounds falling out of the line, *e. g.* benzene, 1-pentene, and chlorinated compounds, are capable to interact, beside always acting nonspecific mode, with one or other specific mechanism.

The role of the specific part of the interaction can be evaluated considering the free energy of adsorption. The values of $\Delta(\Delta G)$ for a pair of adsorbates, benzene

Table 1. Isosteric heat of adsorption ($-\Delta H$/kJ mol^{-1}) and entropy of adsorption ($-\Delta S$/J mol^{-1} K^{-1}) values for named adsorbates on various thermally treated zirconium oxide

Absorbate	523 K		873 K		1173 K	
	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$
Pentane	44.32	113	38.46	106	35.76	98
Hexane	54.07	125	45.74	115	44.70	111
Heptane	70.69	149	54.05	126	53.01	120
Octane	—	—	64.03	142	68.73	146
Cyclohexane	50.79	118	43.66	111	41.58	105
2-Methylbutane	41.12	107	38.05	106	35.34	98
2-Methylpentane	49.92	117	42.62	110	42.62	107
2,2-Dimethylbutane	51.80	122	42.62	111	39.92	103
2,3-Dimethylbutane	51.91	121	42.62	110	41.58	105
2,4-Dimethylpentane	—	—	48.86	118	49.90	117
2,2,4-Trimethylpentane	—	—	54.47	124	54.05	120
Cyclopentene	46.76	118	44.70	116	—	—
Benzene	53.95	119	54.47	124	—	—
Chlorobenzene	—	—	65.49	136	—	—
Bromobenzene	—	—	73.80	147	—	—
Toluene	—	—	60.29	129	63.20	128
1,2-Dichloroethane	40.73	115	45.32	121	—	—
Trichloroethylene	57.07	130	51.35	122	—	—
Tetrachloroethylene	62.21	135	55.72	128	—	—

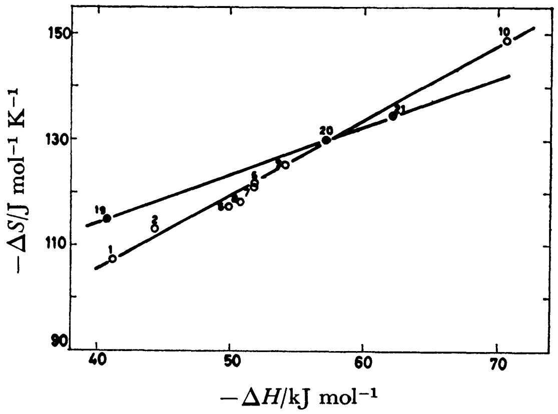

Fig. 5. Plots of ΔS *vs.* ΔH.
19: 1,2-Dichloroethane, 20: trichloroethylene, 21: tetrachloroethylene. Other symbols as in Fig. 2.

and hexane at 473 K, on the zirconia treated at 523, 873, and 1173 K are −2.82, −4.29, and −6.45 kJ mol^{-1}, respectively. These values represent the contribution of three double bonds from benzene ring. It is normal that $\Delta(\Delta G)$ increases with the increasing treatment temperature; such a treatment leads to dehydroxylation of the surface and therefore to the surface activation. The increased $\Delta(\Delta G)$ values are also connected to the thermal treatment which leads to the change of the crystalinity of zirconium oxide.

Empirical dependence of ΔS on ΔH, designated in literature as a compensation effect, is shown in Fig. 5 for the material preheated at 523 K. Nonspecific interacting adsorbates lie on the same straight line, although a separate line can be constructed for the chlorinated compounds. Two separate lines indicate two different types of interactions as pointed out above.

The values of the isosteric heats of adsorption of normal alkanes on zirconium oxide are similar to those obtained on silica.[14] On the other hand, the increment of ΔH for each CH_2 group is much higher when zirconia is used as adsorbent, implying the stronger nonspecific adsorption.

Many problems in the field of GSC thermodynamics remain without definite answers. A complete explanation of the nature of the interactions acting between adsorbate and metal oxides must await further experimentations.

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