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GAS ADSORPTION STUDIES ON ION-EXCHANGED FORMS OF CRYSTALLINE ZIRCONIUM PHOSPHATE

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SUMMARY

Gas-solid chromatography was used to measure the heats of adsorption of eight aromatic and aliphatic adsorbates on crystalline α -zirconium phosphates. Four cation-exchanged phosphates were examined. Evidence was that both aromatic and aliphatic hydrocarbons were physically adsorbed in such a manner as to be screened from the cations in the cavities that are present in the zirconium phosphates. Surface areas are measured to enable entropies to be calculated. Entropy values are used to suggest modes of adsorption on to the crystalline surfaces.

INTRODUCTION

The properties of zirconium phosphates have been the subject of two comprehensive reviews^{1,2}. The major portion of these reviews were devoted to descriptions of the variety of crystalline, "semi-crystalline" and gel phases which can be prepared. Very little is known of the structures of these materials but some of them have the same potential versatility, as porous media, as the zeolite minerals.

The literature contains several publications suggesting the use of zirconium phosphate as a catalyst for the dehydration of alcohols³⁻⁶, the polymerization of ethylene oxide⁷, and the isomerization of cyclohexane to methyl cyclopentene⁶. Other studies refer to the thermal decomposition of an ammonium zirconium phosphate⁸ and the acid properties of a zirconium phosphate surface⁹.

This study uses the technique of gas-solid chromatography to measure the heats of adsorption of aromatic and aliphatic hydrocarbons on crystalline α -zirconium phosphate (α -ZrP). The structure of this adsorbent in its hydrogen form is known and the position of other counter ions can be conjectured^{1,2}. Here the hydrogen, lithium, sodium and potassium exchanged form of α -zirconium phosphates have been used.

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THEORY

Isotherms were constructed directly from elution peaks. The method of Cremer and Huber¹⁰ was used in the manner suggested by Saint-Yrieix¹¹ taking into account the Bechtold correction¹². A computer programme was written to provide (a) a least squares best fit to isotherm data; (b) the slope of appropriate isosteres to calculate the different heats of adsorption, ΔH ; and (c) an interpolation to estimate the free energy of adsorption, ΔG , and the differential entropy of adsorption (ΔS) in the usual manner.

From these experimental values of ΔS , can be calculated ΔS^0 representing the difference in differential molar entropy between the three dimensional adsorbate in its standard state and adsorbed standard states. This can be done for the two models of localized and non-localized adsorption, described by de Boer and Kruyer¹³, using the equation of Everett¹⁴.

Thus for immobile (site) adsorption

$$-\Delta S_i^0 = -\Delta S - R \ln \theta / (1 - \theta) \quad (1)$$

and for mobile adsorption, when the adsorbate is considered an ideal two-dimensional gas,

$$-\Delta S_m^0 = -\Delta S - R \ln A^0 / A \quad (2)$$

where $\theta = \omega M / a \rho_T t_p$, $A^0 =$ standard molecular area, $A =$ area per molecule, $\omega =$ moles of adsorbate per gram of adsorbent, $M =$ molecular weight of adsorbate, $a =$ surface area of adsorbent, $\rho_T =$ density at temperature T , and $t_p =$ thickness of adsorbate molecule¹⁵.

The value $A^0 = 4.08 T \times 10^{-12} \text{ m}^2$ was used throughout and A was determined from experimental values for a . Values of $-\Delta S_i^0$ and $-\Delta S_m^0$ were compared to ideal values for the two models. If the system behaved as the model of entropically ideal site adsorption, then $-\Delta S_i^0$ calculated from $-\Delta S$ with various amounts adsorbed should be independent of surface concentration of adsorbate and its value should represent the total loss of translational entropy.

So when the localised entropy of the adsorbed layer (${}_a S_{loc}^0$) is zero at $\theta = \frac{1}{2}$ we can expect

$$-\Delta S_i^0 = {}_g S_{tr}^0 \quad (3)$$

where ${}_g S_{tr}^0$ is the translational entropy of the adsorbate.

If however the system was one of entropically ideal mobile adsorption $-\Delta S_m$ should still be independent of adsorbate concentration and should be given by

$$-\Delta S_m^0 = {}_g S_{tr}^0 - {}_a S_{tr}^0 \quad (4)$$

where ${}_a S_{tr}^0$ is the translational entropy of an ideal molar gas. ${}_g S_{tr}^0$ and ${}_a S_{tr}^0$ can be calculated¹⁴:

$${}_g S_{tr}^0 = R \ln (M^{3/2} \cdot T^{5/2}) - 2.30 \quad (5)$$

and

$${}_a S_{tr}^0 = 2/3 {}_g S_{tr}^0 + 1.52 \log T - 3.04 \quad (6)$$

(Note. Everett¹⁶ has pointed out that

$${}_a S_{tr} = {}_a \bar{S}_{tr} + R \quad (7)$$

where ${}_a \bar{S}_{tr}$ = standard differential molar entropy of an ideal two-dimensional gas and this was taken into account.)

EXPERIMENTAL

Ion-exchanged samples were prepared from the hydrogen form of α -zirconium phosphate. Full details of their composition and characterization have already been published¹⁷.

Crystalline zirconium phosphates were crushed and sieved. Aliquots of about 10 g of the 60–85 BSM fraction were used to pack gas chromatographic columns. Packing was carried out without undue agitation to avoid deaggregation of the 60–85 fraction. Packed columns were conditioned for 24 h at temperatures previously defined by thermogravimetric analyses¹⁷. This conditioning was repeated to constant weight.

Preliminary experiments showed that (a) a linear relationship existed between peak area and sample size and (b) the isotherms obtained were unaffected by changes in carrier gas flow-rate.

The chromatograph used was a Pye 104 Model 34 with a katharometer detector. The carrier gas was Mineral Helium (BOC, Lancs., Great Britain) dried by a molecular sieve 4A column. When various sample sizes were eluted from any column at identical conditions of gas flow-rate, temperature, etc., the elution peaks were calculated from any elution peak¹⁸ since the diffuse edge of the peak was thus reproducible.

Surface areas were measured by an adaptation of the method of Kuge and Yoshikawa¹⁹. The method involves the "imposition" of a gas-liquid peak onto a gas-solid peak to give an overall peak shape as shown in Fig. 1. Interpretation of the concentration up to point X should correspond to the amount of adsorbate required to form a monolayer and by use of the molecular area of the area of the adsorbate the surface area can be obtained. The procedure was as follows.

Elution peaks of the type described were obtained and the number of moles/g adsorbent (n_x) corresponding to the point X (Fig. 1) calculated. Assuming the adsorbate to be adsorbed as a liquid film the volume of liquid (V_x) corresponding to n_x was calculated from information of the bulk density of the liquid at the temperature of the elution. This quantity (V_x) was divided by the probable thickness (tp) of the adsorbed layer and the surface area obtained.

Surface areas were also calculated by a BET nitrogen method²⁰ for comparison.

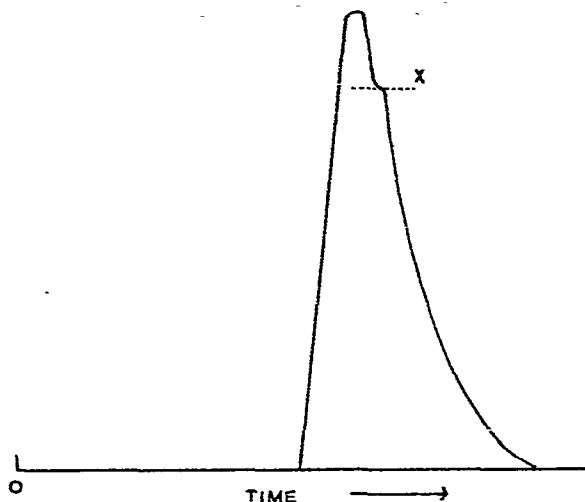


Fig. 1. Asymmetric gas-solid chromatography elution peak used for surface area calculations.

RESULTS

Surface area measurements are presented in Table I. A typical family of isotherms is shown for benzene adsorption on α -zirconium phosphate in its hydrogen form (Fig. 2). The example is extended to show ΔG and ΔH values (Fig. 3) as a function of surface coverage. Table II summarizes the data obtained for all the adsorbate-adsorbent systems studied. Figs. 4-10 show entropy data.

TABLE I
SURFACE AREA MEASUREMENTS

Adsorbent	Adsorbate	Assumed orientation of adsorbate molec. on surface	Surface area by chromatographic method (m^2/g)	BET surface area (m^2/g)
α -ZrPH	<i>n</i> -hexane	horizontal	10.8	32.5
	cyclohexane	horizontal	10.2	
	1-hexene	L-shaped C_4 thick	10.4	
	benzene	vertical	10.0	
α -ZrPLi	<i>n</i> -hexane	horizontal	23.8	42.2
	cyclohexane	horizontal	26.3	
	1-hexene	L-shaped C_3 thick	23.0	
α -ZrNa	<i>n</i> -hexane	horizontal	13.9	23.6
	cyclohexane	horizontal	14.1	
	benzene	vertical	14.3	
	1-hexene	L-shaped C_3 thick	13.3	
	cyclohexane	vertical	14.2-15.8	
α -ZrPK	benzene	vertical	10.4	20.1
	cyclohexane	horizontal	10.0	
	<i>n</i> -hexane	horizontal	10.2	

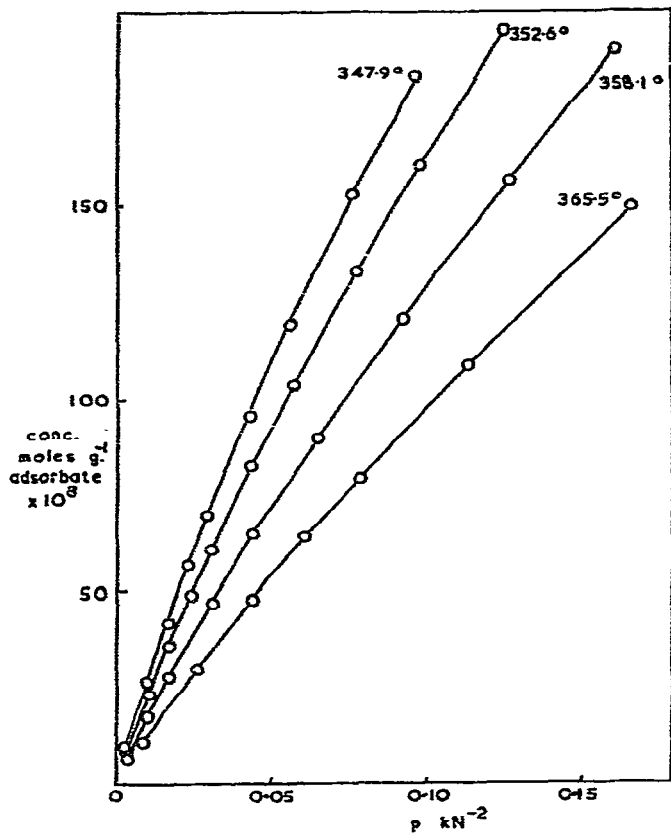


Fig. 2. Isotherms of benzene on α -ZrPH.

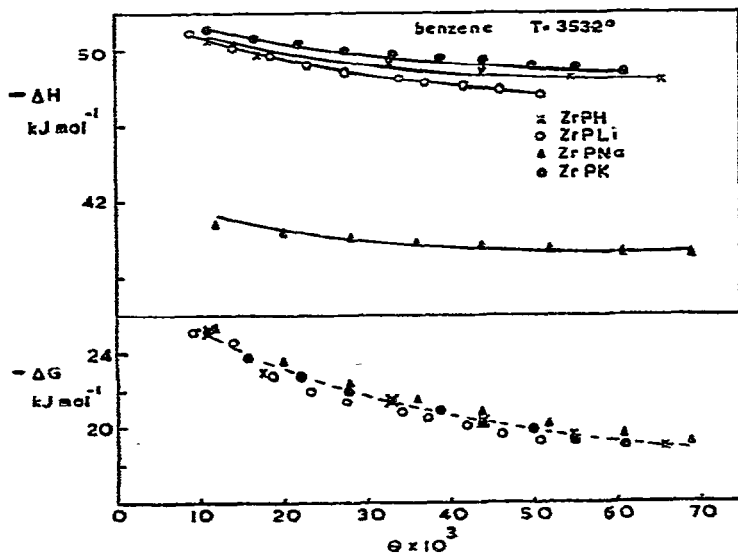


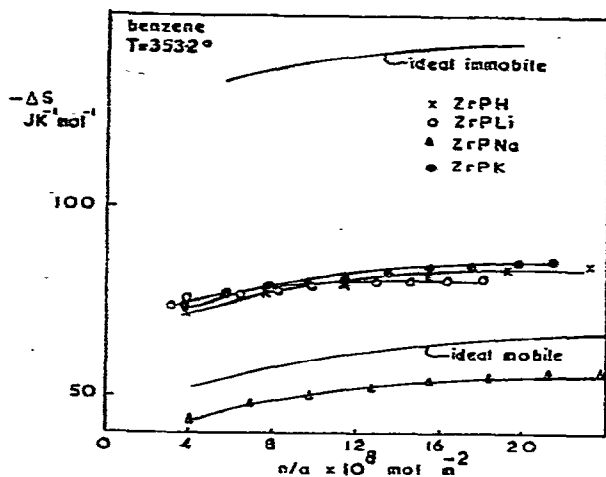
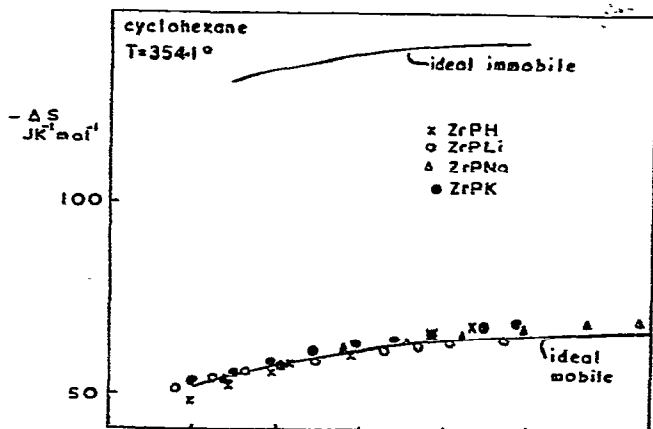
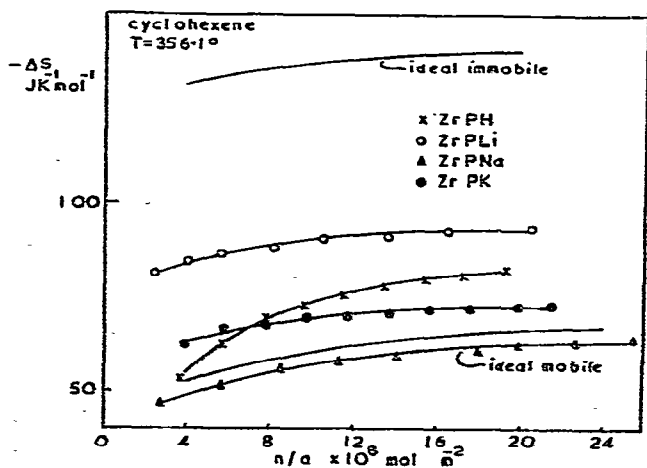
Fig. 3. Variation of ΔG and ΔH with surface coverage for benzene on ion-exchanged α -zirconium phosphates.

TABLE II
THERMODYNAMIC PARAMETERS OF ADSORPTION

Adsorbent	$-\Delta H$ (kJ/mol) at $\theta = 25 \cdot 10^{-3}$										
	Adsorbate										
	Benzene	Toluene	Ethylbenzene	Cyclohexane	Cyclohexene	n'-Hexane	1-Hexene	n-Heptane	n-Octane		
α -ZrPH	49.4	59.0	62.8	35.2	45.6	37.7	48.1	43.6	46.9		
α -ZrPLi	49.0	—	—	35.6	50.6	39.8	48.5	—	—		
α -ZrPNa	40.2	—	—	36.4	39.4	36.4	43.9	—	—		
α -ZrPK	50.2	—	—	36.8	41.9	43.1	47.7	—	—		
$-\Delta G$ (kJ/mol) at $\theta = 25 \cdot 10^{-3}$	21.8*	23.4**	23.8**	14.2*	18.4*	16.6*	20.9*	17.2**	18.8**		
Isostere temp. range	347-366	378-393	398-415	341-366	347-366	335-353	335-353	365-383	392-408		

* Average value (± 1 J/mol) for all adsorbents.

** Measured on α -ZrPH.

Fig. 4. Variation of $-\Delta S$ with n/a for benzene on α -ZrP.Fig. 5. Variation of $-\Delta S$ with n/a for cyclohexane on α -ZrP.Fig. 6. Variation of $-\Delta S$ with n/a for cyclohexene on α -ZrP.

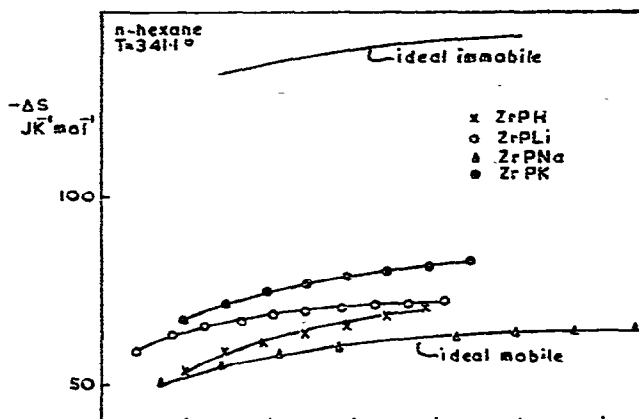


Fig. 7. Variation of $-\Delta S$ with n/a for *n*-hexane on α -ZrP.

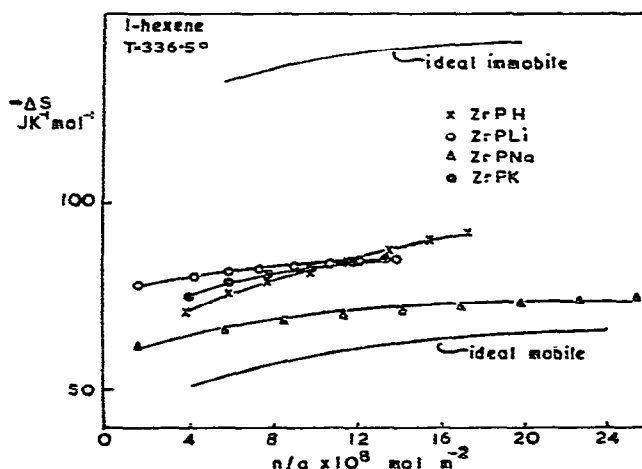


Fig. 8. Variation of $-\Delta S$ with n/a for 1-hexene on α -ZrP.

DISCUSSION

Surface area

Since surface area plays an important role in determining θ , A^0/A and hence the various entropy values, a pore volume was calculated as described by Gregg and Sing²¹. The value was more than one hundred times less than a theoretical pore volume calculated from the X-ray interlayer spacings¹⁷. This seems to imply that the adsorptions observed were not taking place in micropores.

At first sight, it seems that entropy calculations might be incorrect if a wrong surface orientation is chosen for calculations (*i.e.* tp will be wrong). It can be demonstrated that a maximum variation of only $\pm 4 \text{ J/}^\circ\text{K}$ arises between the cases of a benzene molecule (a) lying flat ($tp = 340 \text{ pm}$) or (b) standing on "an edge" ($tp = 680 \text{ pm}$).

Table I shows the orientations used in entropy calculations the choice of

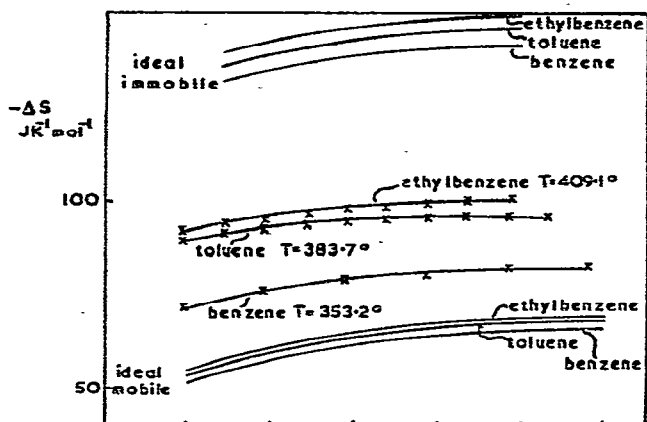


Fig. 9. Variation of $-\Delta S$ with n/a for benzene, toluene and ethylbenzene on α -ZrPH.

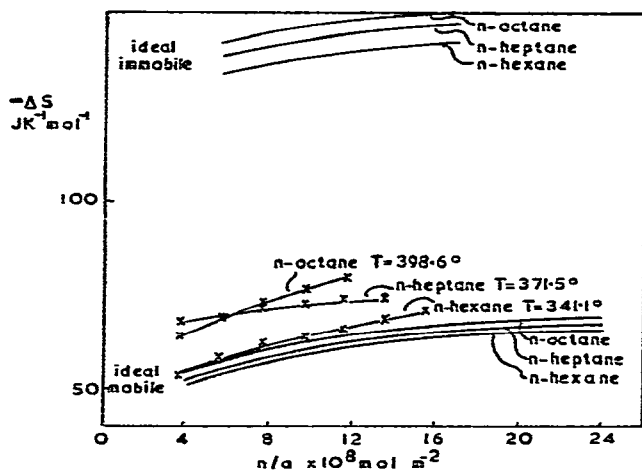


Fig. 10. Variation of $-\Delta S$ with n/a for *n*-octane, *n*-heptane, *n*-hexane on α -ZrPH.

orientation being that to give consistent results. It can be seen that the figures from the chromatographic method are at variance with those from the BET technique.

Heats of adsorption

Small changes in ΔH with surface coverage (e.g. Fig. 3) indicated a regular surface with little or no evidence of surface heterogeneity at the lower coverages studied. All the values measured were higher than the adsorbate latent heat of vaporization but not sufficient to suggest that anything other than physical adsorption was being observed. The adsorbates examined were from the classification of Kiselev²², viz. (a) molecules capable only of non-specific action and (b) molecules capable of non-specific and specific interactions. Kiselev and Lopatkin²³ also suggest that the same specific and non-specific terminology be applied to adsorbents and, by their definition, the zirconium phosphates are all non-specific. Their expandable layer

structure and "zeolitic" water content might be expected to give specific interactions, but the critical cavity dimensions in the non-expanded forms of α -zirconium are about $260 \text{ pm}^{1.2}$, which, in a zeolite structure, will exclude all molecules except water and ammonia.

Entropies of adsorption

Lithium, sodium and potassium forms (see Figs. 4-8). All adsorbates (except 1-hexene) have close to complete mobility on the sodium zirconium phosphate, indeed cyclohexane and benzene are "super-mobile"²⁴, i.e. the adsorption is so weak that the entropy associated with the vibration replacing the lost degree of translational freedom is too strong to neglect.

In both the lithium and potassium forms entropy losses above the ideal state are observed and can be ascribed to lost degrees of rotational freedom. As apparently there are no direct ion-adsorbate interactions, these variations in entropy must arise from changes in surface potential energy.

Hydrogen form (Figs. 9 and 10). Here the entropy changes offer some indication of the form of restriction in degrees of freedom. Benzene, toluene and ethylbenzene are increasingly restricted. This is Kemball's anchoring effect²⁴, that substituent groups have on an aromatic nucleus. Again, in the series *n*-hexane, *n*-heptane, *n*-octane, there is an increase of entropy equivalent to about $6 \text{ J} \cdot ^\circ\text{K}^{-1} \cdot \text{mol}^{-1}$ per carbon atom increase in the hydrocarbon chain. Kemball²⁵ calculates that an increase from C_6 to C_7 should provide an additional entropy of about $20 \text{ J} \cdot ^\circ\text{K}^{-1} \cdot \text{mol}^{-1}$, so, for these adsorbates on α -hydrogen zirconium phosphate, no new restrictions to bond rotation occur as chain length increases. Increases in moments of inertia for overall rotation must be the main contributors to the entropy losses.

Generally the presence of a double bond causes an increase in restriction in comparison to the adsorption of the unsaturated homologue. This generally is true for all the adsorbents studied (e.g. compare Figs. 4 and 5).

Free energies of adsorption

The ΔG values for a particular adsorbate are nearly independent of adsorbent. This supports the earlier suggestion that non-specific adsorption occurs and that the alkali metal ions are screened from the adsorbate molecules.

CONCLUSION

Adsorption on α -zirconium phosphates is at the surface and not within zeolite-like cavities within the structures. It seems that only oxygen-containing molecules have strong interactions with zirconium phosphate surfaces. This concurs with their potential catalytic usage³⁻⁷. Attempts to separate alcohols by gas chromatography have not been possible owing to these strong interactions²⁶.

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