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Zeolites: Coneyers of Non-Euclidean Geometry

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The increasing use and application of zeolites merit an intensive effort toward attaining a more profound understanding of the nature of the physicochemical features responsible for the exceptional performance of zeolites applied to different areas of chemistry such as catalysis and cracking. By and large, the scientific community has resorted to conventional, or ad hoc, models to explain this remarkable activity. Included among these are lengthy discussions of adsorption on other surfaces, van der Waals, electrostatic and dispersion forces, quadropole interactions, or different combinations of the latter. With the introduction of synthetic zeolites, i.e., aluminium-free and/or aluminium-deficient, the confusion was enhanced. The noninsertion or the removal of the negatively charged $[AlO_4]^-$ unit eliminated the pore-blocking effect of the positively charged counter-ion and altered the impact of electrostatic forces. Furthermore workers in the field are frequently forced to include additional ad hoc effects such as ill-defined structural defects, super-acid sites, or the occasional "hot-spot." As a consequence the literature on zeolite chemistry is ambiguous as to the origin of the forces exerted on sorbate molecules.

In the beginning of this decade in a series of papers, Andersson and Hyde (*1–4*) convincingly showed that the problem of zeolite properties and reactivities could be treated by including non-Euclidean geometry. As will be shown (*vide infra*) the concept of intrinsic curvature and its extension, the average Gaussian curvature, provide the means for explaining zeolite–sorbate interactions hitherto not properly accounted for.

A recent article (*5*) dedicated to the adsorption of different hydrocarbons on highly dealuminated zeolites contains a substantial amount of information incorrectly interpreted, largely due to the inadequacy of conventional models. However, if we allow for the presence of highly curved surfaces most of the problems disappear. For instance, if the differential heats of adsorption of a series of hydrocarbons, nC_2–nC_{10}, on the highly dealuminated zeolite US-Ex (faujasite group) are plotted against the loading on the zeolite the heat curve initially (i.e., at loadings <0.2 mmol g^{-1}) falls steeply, from a vaguely determined zero-loading value, passes through a minimum at $\simeq 0.2$ mmol g^{-1}, whereupon it steadily rises to a maximum at >1.0 mmol g^{-1}, after which it levels off (Fig. 1).

The Gaussian curvature (K) of a surface is defined as the product of the principal curvatures; the latter are defined as the inverse of the radii of the circles that most closely approximate the curves that are obtained when a plane through the surface

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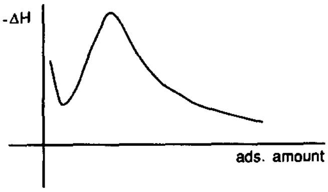

FIG. 1. Schematic representation of hydrocarbon adsorption on US-Ex.

normal is rotated around that normal. For a minimal surface the principal curvatures have the same values but opposite signs in its every point, hence $K < 0$. For a given surface element K in every point can be determined and the integral Gaussian curvature can be calculated. When the latter is divided by the area of the surface element the average Gaussian curvature is obtained. According to Thomasson *et al.* (*6*) the adsorptive properties of a non-Euclidean surface are determined by the average Gaussian curvature of the surface. That is, the total van der Waals forces exerted by the various structural elements establishing the surface are focused into a force field that runs parallel to the original surface. A highly symmetric structure such as faujasite can then be envisaged as a force field matrix enabling sorbate molecules to travel nearly adiabatically along principal lines of curvature, i.e., on paths continuously permeating the entire structure.

A translation of this situation into physical terms implies a state of aggregation between that of a gas and a liquid, i.e., a quasi-liquid. This picture is, of course, only valid at very low loadings. At higher loadings, due to intermolecular crowding, molecules will be displaced toward the sorbent surface, out of the force field focus, where interception by sites of maximum Gaussian curvature will prevail; in physical terms, this is analogous to solidification.

For the heat *versus* loading curves the following interpretation can then be formulated: the first part of the curve, i.e., the descent at loadings of less than 0.2 mmol g^{-1} is attributable to sorbent bulk inhomogeneity. In the preparation of US-Ex, structural aluminium is leached out from NaY by acid percolation, followed by heat-curing of the framework (*7*). As can be seen from the analysis of the sample, aluminium removal is not complete; the silicon to aluminium ratio is approximately 95 : 1, indicating the presence of structural domains resembling native NaY. Furthermore, during the heat-curing one anticipates that recrystallization takes place. Since no extraneous silicon is added this process relies on chance presence of SiO_2; thus, framework curing can be severely hampered leading to the formation of, e.g., small-ring zeolitic entities. Both NaY and small-ring zeolites, e.g., sodalite, exhibit higher average Gaussian curvature than US-Ex.

Consequently, the first part of the heat curve has no bearing on the remainder. It is simply condensation on non-US-Ex zeolitic entities, the higher curvature of which attracts the sorbate molecules entering initially. Thus, the minimum at ≈ 0.2 mmol g^{-1} results from the intersection of the descending heat curve ascribable to non-US-Ex adsorption and the ascending heat curve of US-Ex. In terms of the image of US-Ex as a force field matrix the heat curve should have the attributes that are actually found. Deconvolution of the heat curve, i.e., removal of the non-US-Ex portion, yields a plateau from zero loading to ≈ 0.2 mmol g^{-1}, implying that the sorbate molecules travel along the paths determined by the force field matrix. There is no intermolecular energy exchange, only a relatively low energy exchange with the sorbent, which depends on molar quantities rather than molecular size. When the loading is increased the heat curve ascends steeply, larger molecules yielding a steeper slope. This implies that sorbate molecules exchange energy, i.e., the number of molecules contained in the force field matrix is increased, thereby enhancing the probability of intermolecular contact, which is then transferred to the sorbent through solidification at the saddle points of maximum Gaussian curvature. At loadings of >1.0 mmol g^{-1} the heat curve reaches a maximum indicative of a phase transition, i.e., a transition from a solid-resembling state to a liquid state. The final descent reflects a situation where intermolecular energy transfer dominates as compared to sorbate–sorbent energy exchange. This latter portion of the heat curve is determined by the large volume available in faujasite zeolites. Entropy measurements fully account for the related phase transitions.

If this treatment is extended to a cyclic structure cyclohexane behaves analogously to *n*-hexane. If one allows for the fact that a cyclic structure may find it impossible to align itself as perfectly to a curved surface, thereby lowering the maximum of the heat vs loading curve, as compared to a straight-chain compound, the overall features are identical.

Silicalite, a zeolite of the pentasil type with narrower pores, i.e., higher average Gaussian curvature, exhibits somewhat different behavior. First, the synthetic procedure creates less distortion of the framework, as evidenced by the absence of a steep descent in the low-loading region of the heat curve. Second, the high curvature, coupled with lack of symmetry, when compared to faujasite, obliterates the opportunity to maintain a force field matrix, except perhaps in the intersection of the channels. Obviously, this will bring about solidification, essentially without transition from a quasi-liquid state of aggregation. Third, the narrow channels cannot lodge a sufficient number of molecules to allow liquefaction, thus explaining the absence of a maximum of the heat curve. This reasoning is fully substantiated by entropy measurements.

In conclusion, we believe that regarding zeolites as conveyers of non-Euclidean geometry can provide a powerful means of understanding phenomena encountered in zeolite chemistry. We also believe that application of this model will enable researchers to make intelligent and fertile predictions regarding framework composition and the outcome of chemical reactions.

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References

1. S. Andersson, S. T. Hyde, and H. G. von Schnering, *Z. Kristallogr.* **168,** 1 (1984).
2. S. T. Hyde and S. Andersson, *Z. Kristallogr.* **168,** 221 (1984).
3. S. T. Hyde and S. Andersson, *Z. Kristallogr.* **170,** 225 (1985).
4. S. T. Hyde and S. Andersson, *Z. Kristallogr.* **174,** 225 (1986).
5. H. Stach, U. Lohse, H. Tamm, and W. Schirmer, *Zeolites* **6,** 74 (1986).
6. R. Thomasson, S. Lidin, and S. Andersson, *Angew. Chem.* **99**(10), 1056 (1987).
7. U. Lohse, E. Alsdorf, and H. Stach, *Z. Anorg. Allg. Chem.* **447,** 64 (1978).