

Heats of Adsorption of Hydrocarbons on Zeolite Surfaces: A Mathematical Approach

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The role of electronic polarizabilities in dealing with the phenomenon of molecular adsorption and catalysis by zeolites has been discussed in this work. Making use of the principles of periodic minimal surfaces of crystalline materials and rules of atomic connectivities of zeolite structures, an expression has been derived to evaluate heats of adsorption of hydrocarbons interacting with the surfaces of zeolites that reads $\Delta H = \alpha_M \cdot \beta \cdot \gamma + \theta_f$, where α_M is the average polarizability of hydrocarbons, β and θ_f are the constants, and γ the average curvature of the zeolite surface. After determining the polarizabilities of hydrocarbons by a quantum mechanical method and establishing the magnitudes of the curvatures of surfaces of zeolites by differential geometrical approach, the formalism has been applied to evaluate heats of adsorption of C_1 – C_8 hydrocarbons on the typical surfaces of MOR, FAU, ZSM-5, and silicalite zeolites. The agreement between theoretical and experimental values of heats of adsorptions of paraffins, naphthenes, olefins, and aromatics has been found to be very good and compares fairly well with those obtained from experimental methods as well as derived by other theoretical methods. The applicability of the data so generated has been demonstrated in estimating the driving force of cracking (activation energy, E) following the Evans–Polyani procedure in the case of n -paraffins interacting with ZSM-5 surface. The data so generated has been used to explain negative activation energy for cracking observed for n -hexadecane and higher alkanes (C_{16} effect).

I. INTRODUCTION

In fundamental catalysis, much interest is attached these days to study the properties of zeolites,¹ the nature of interaction of hydrocarbons with their surfaces,² and phenomenon of adsorption, activation, and cracking through molecular simulation and other theoretical approaches.^{3–8} Therefore, in this work, an attempt has been made to establish that the heats of adsorption of hydrocarbons interacting with the surfaces of different zeolites depends not only on the curvatures of zeolite surfaces and polarizabilities of hydrocarbons but also on the atomic connectivities of zeolite frameworks by defining the “residual atomic polarizability degree of freedom”, ndf , associated with each atom in the zeolite structure, similar to the topological density, TD_{2-5} , as defined by Barthomeuf³ in the case of ZSM-5, mordenite, faujasite, and silicalite, and shown in Figure 1. Hence, in the present study we will focus mainly on the nature of adsorption and activation of hydrocarbons on zeolitic surfaces. Such data on adsorption and activation over, for example, n -alkane on ZSM-5, would be of value to invoke cracking rates and pathways of cracking reactions of hydrocarbons important in the processing of distillate fuels and lube dewaxing of petroleum to lower the pour point for winter uses and high altitude flights. Owing to this fact, much interest had been attached these days to study adsorption phenomenon of hydrocarbons on zeolite surfaces both by theoretical^{6–8} and experimental methods^{9–12} and also had been a matter of serious concern in the past^{13–15} and forms the focus of current studies^{16–19} as well as including the present one. Such studies would be of value in establishing the quantitative structure–activity relationship (QSAR) in crystalline solids such as zeolites as it has been shown useful

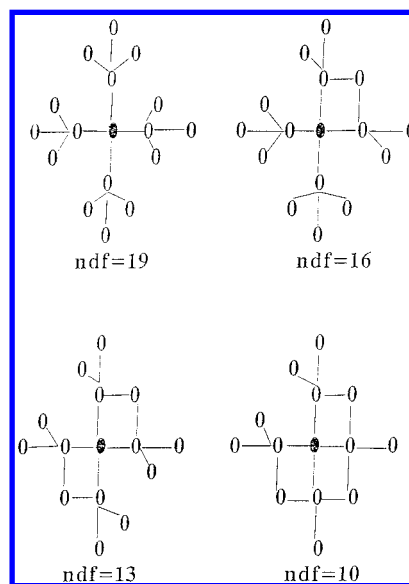


Figure 1. Scheme for the connectivity of atoms (O) around a central atom (C) and polarizability degrees of freedom (ndf) of atoms in zeolites.

in the other case of other inorganic, metal crystals to cell membrane and biopolymer.¹⁸

II. POLARIZABILITY MODEL AND MOLECULAR ADSORPTION

Discussions are already available in the literature on the concept of polarizability in zeolites science and acid catalysts.^{20–26} As such adsorption is considered as the process that depends on the fraction of surface that is bare.

On approaching the surface, each atom or molecule encounters an attractive potential that ultimately will bind it to the surface under proper circumstances. Hence, adsorption involves trapping of atoms or molecules incident on the surface and is always an exothermic process. Hence rules of surface physics must apply. Throughout this paper, we propose a "polarizability model" to deal with the problem of adsorption process of hydrocarbons on acid zeolite surfaces. It is well-known that polarizability is one of the most fundamental electrical properties of molecules that, during any chemical event, makes charge-transfer possible through electronic polarization of bonds or in describing intermolecular potentials. The long weak bonds of the transition state are more polarizable than the full bonds of substrate and products. In such processes the polarizability term dominates. Hence, it is very important to compute polarizability of interacting molecular systems.

The average polarizability of the molecules, $\alpha_M = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, $= 1/3(\sum \alpha_{||} + 2\sum \alpha_{\perp})$, could be determined with the help of the delta function potential model.¹ Accordingly at every nucleus of the atom, there exists a potential whose properties could be described as under

$$\delta(x) = 0 \text{ when } x \neq 0 \quad (1)$$

$$\delta(x) = \infty \text{ when } x = 0 \quad (2)$$

and

$$\int_{-\infty}^{+\infty} \delta(x) dx = 1 \quad (3)$$

Thus, the potential is zero everywhere except at the delta function positions where it is infinite in such a way that

$$A_{1g} \int_{-\infty}^{+\infty} (x - 1/2a) dx = A_{1g} \quad (4)$$

$$A_{2g} \int_{-\infty}^{+\infty} (x + 1/2a) dx = A_{2g} \quad (5)$$

where g is the unit delta function of atomic hydrogen and a is the delta function spacing between two nuclei. The solution of the Schrodinger equation for the molecular problem yields separate wave function for the bond and correspondingly the i th bond wave function is obtained. Using these wave functions the parallel component of polarizability is obtained, using variational method, and the perpendicular component is computed by considering residual atomic polarizability degree of freedom and atomic polarizabilities of atoms. And finally the average polarizability is computed using additivity principle of bonds.

In the variational treatment adopted in this work for the computation of average polarizability, α_M , of hydrocarbon in terms of coordinates of motion of nuclei is given in¹

$$\alpha_M = \frac{1}{3} \left\{ \sum_{ij} \frac{4nA_{12}\sigma}{a_0} [\langle x^2 \rangle]^2 + ndf \sum_j X_j^2 \alpha_j \bar{n} \sum_j X_j^2 \right\} \quad (6)$$

In the above equation the first term stands for parallel component of polarizability and the second term stands for the perpendicular component. The ndf is the residual atomic polarizability degree of freedom, where n is bond order, A_{12} the reduced delta-function strength, σ the covalency factor, α_i the atomic polarizability, and X_j the electronegativity of

the j th atoms. The term $\langle x^2 \rangle$ represents the probability amplitude of electrons expressed in terms of internuclear distance R as

$$\langle \bar{X} \rangle = \frac{R^2}{4} + \frac{1}{2C_{R12}^2} \quad (7)$$

where R is the internuclear distance at the equilibrium configuration, and

$$C_{R12}^2 = (n_1 n_2 N_1 N_2)^{1/4} (A_1 A_2)^{12} \quad (8)$$

where A_i , n_i , and N_i ($i = 1, 2$) represent the δ -function strength, the principal quantum number, and the number of electrons making contribution to the binding, respectively.

The basic postulates of the polarizability model adopted for adsorption studies are that (i) all the atoms in the zeolite structure are polarizable and possess three atomic polarizability degrees of freedoms. When a bond is formed by two atoms, at least one of the polarizability degree of freedom is lost which contributes to the perpendicular component of the polarizabilities of the molecular system and is made responsible to consider interaction with adsorbing molecules, (ii) any hydrocarbon molecule making contact with the zeolite surface gets polarized under the influence of electric field associated with the channels of zeolites whose polarizabilities could be computed by the procedure described earlier, and (iii) the surface of zeolite is not smooth but has curvature, either convex ($-$) or concave ($+$) which could be determined by the rules of geodesic mathematics.¹⁸ The hills and elevations forming concave surfaces repel the molecule, while valleys and holes forming the convex surface attract them. In light of rules contained in postulates (i–iii), and making use of Gauss–Bonnet transformation of the geodesic mathematics applicable to the geodesic surfaces of zeolites, it is possible to extract information on the heats of adsorption. One of the important equations in differential geometry is the Gauss–Bonnet equation

$$\int_{ABC} K ds = A + B + C - \pi \quad (9)$$

Here, A , B , and C are the interior angles in the geodesic triangle, and average curvature K_{av} is defined as under

$$K_{av} = \int \int K ds \text{ per surface unit} \quad (10)$$

where ds is the surface element. The integral curvature measured is the intrinsic difference between a region of the surface and a region of the plane or in other words how much curvature a region of a surface contains (based on the convention that a plane has zero curvature). In above equation, $\int \int K ds$ is extremely simple to calculate. For a tetrahedral saddle it is $-2/3\pi$, and if the surface area is calculated for such a saddle by numerical integration, for a typical faujasite structure of unit cell dimension $a = 24.30$ Å its K_{av} is equal to $-0.0444/\text{\AA}^2$. Similarly, for other zeolite structures, the K_{av} values could be calculated or extrapolated from measured heats of adsorption.

Considering the above facts, it is worth quantifying initial heat of adsorption, ΔH , in terms of curvature of zeolite surface, γ ($= K_{av}$), and the delta function polarizability, α_M ,

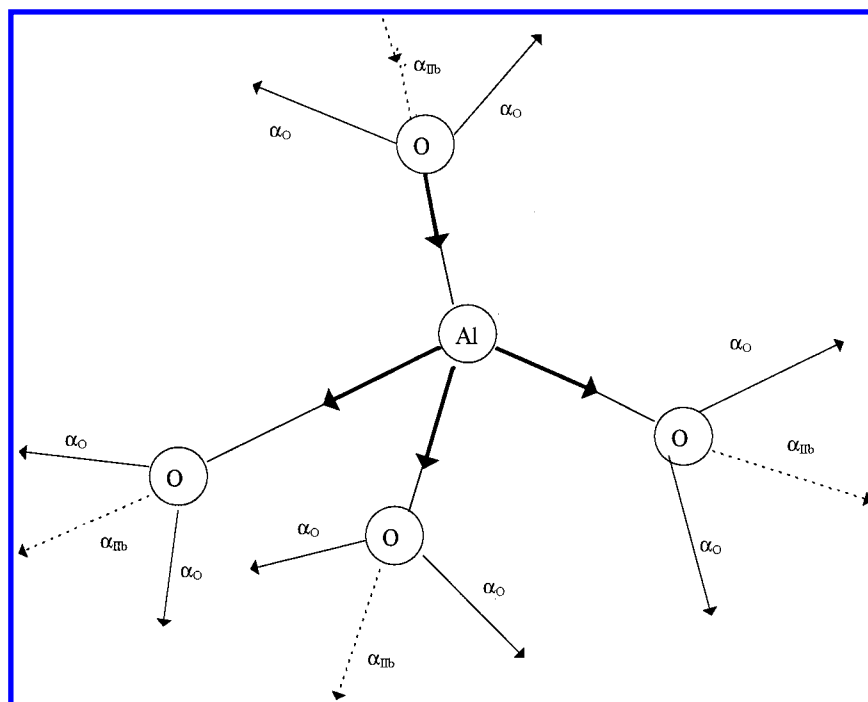


Figure 2. Residual atomic polarizability degrees of freedom (ndf) for a TO_4 tetrahedral unit in zeolites ($\text{ndf} = 3N - 2\text{nb}$).

of interacting hydrocarbons with zeolite surface (note that molecules experience an attractive force on the surface) by the relation

$$\Delta H = \alpha_M \cdot \beta \cdot \gamma + \theta_f \quad (11)$$

where $\beta = \text{ndf}$ (equal to $3N - 2\text{nb}$) defined in Figure 2, N is the number of atoms, and nb is the number of bonds in the zeolite structure. On this basis, Thomasson et al.³³ verified the measurements of Rees³⁴ and Stach et al.^{24,35} on the heats of adsorption of hydrocarbons on US-Ex and silicalite zeolites, and we have extended the study on C_1 – C_8 n -alkanes on ZSM-5, silicalite, mordenite, and faujasite structures.¹⁹ However, we have extended this study to other hydrocarbons viz. olefins, aromatics, and naphthenes. Having computed the values of heats of adsorptions, the activation energy, E , (energy barrier to the reaction), has been verified by Evans–Polanyi method³⁶ to explain C_{16}^+ effect in the case of n -alkane/ZSM-5 interfacing.

III. RESULTS AND DISCUSSIONS

In Table 1, the heats of adsorptions of hydrocarbons obtained from the polarizability model have been compared with the experimentally measured values^{37–41} in the case of ZSM-5, silicalite, FAU, and mordenites surfaces, and data trend has been displayed in Figure 3. Data on heat of immersion studies are available, from which the idea of heat of adsorption could also be gained. To obtain heats of immersion, $\Delta_i H$, Messow et al.⁵¹ took into account the limiting adsorption values n^s

$$\Delta_i H = \frac{\Delta_i H (\text{J g}^{-1})}{n^s (\text{mol g}^{-1})} \quad (12)$$

The limiting adsorption values could be measured with a special pycnometer. Further using the rule of Hess it is possible to evaluate the heat of adsorption, $\Delta_A H$, from the

heat of immersion, $\Delta_i H$, and heat of condensation, $\Delta_L H$, by the relation $(-)(\Delta_A H) = (-)\Delta_i H + (-)\Delta_L H$ (such data has been collected in Table 2). Our data on n -alkane/ZSM-5 compares reasonably well with the values reported by Stach for ethane and butane and Messow et al.⁵¹ for C_5 to C_{17} n -alkane (see Table 2 footnote). This again establishes the basic soundness of our adopted model and calculations. Experimental heats of adsorption data of n -alkanes on silicalite are available for comparison with our results: C_1 – C_4 alkane/silicalite by Titiloye et al.⁸ and C_5 – C_{10} alkanes/silicalite by Sun et al.⁴¹ (see Table 1). In the case of C_1 – C_4 alkanes, our data are close to the experimental values quoted by Titiloye et al.⁸ in contrast to their own Monte Carlo calculations results. Similarly, in the case of C_5 – C_{10} alkanes, the recently measured data by Sun et al.⁴¹ are close to our results than computed values of Titiloye et al.⁸ showing basic soundness of our adopted model. In search of a better correlation, we have discovered that the heats of adsorption of hydrocarbons are linearly related to the average polarizabilities of paraffins, the residual atomic polarizability degree of freedom of zeolite structure which accounts for inductive effect of one atom on the other, and the curvature of zeolite surface, see Figure 4, wherein we have extended our studies on a relatively higher alkanes/ZSM-5 system with the view to invite attention of experimentalists to work for higher alkane adsorption and other hydrocarbons lying in the same carbon range.

As suggested by Haag,⁴⁹ it is proper to separate out the apparent activation energy into its constituent elements, namely the temperature dependence of the intrinsic activation energy, E_0 , and that of the sorption constant, which is the heat of sorption, ΔH . Therefore, one can obtain the heat of sorption enthalpies in ZSM-5 for the paraffins studied (see Table 2). They are very similar to the data published in the literature.⁵⁰ Haag⁴⁹ further explains with $k = A \cdot \exp(-En^*/RT) = A \cdot \exp(-E_0/RT) \cdot \exp(-\Delta H/RT)$, where R is the gas constant and T the temperature and obtains $En^* = E_0 + \Delta H$.

Table 1. Heats of Adsorption (kcal/mol) of Hydrocarbons on ZSM-5, Silicalite, Faujasite, and Mordenite

| hydrocarbon | ZSM-5 | | | silicalite | | | faujasite | | | mordenite | |
|---|-----------------|--------------------|-------|-----------------|--------------------|--------------------|-----------------|-------------------|--------------------|-----------------|--------------------|
| | PW ^g | theo ^b | exptl | PW ^g | exptl ^d | exptl ^d | PW ^g | theo ^b | exptl ^b | PW ^g | exptl ^a |
| Paraffins | | | | | | | | | | | |
| CH ₄ | 6.02 | 5.67 | | 4.12 | 5.43 | 4.87 | 5.30 | 4.85 | | 6.40 | 6.1 ± 0.5 |
| C ₂ H ₆ | 8.40 | 9.97 | 8.97 | 6.27 | 8.93 | 7.84 | 6.94 | 6.14 | 5.09 | 8.80 | 8.0 ± 0.3 |
| C ₃ H ₈ | 10.92 | 16.00 | | 8.53 | 12.10 | 9.53 | 8.66 | 9.61 | 6.46 | 11.33 | 10.0 ± 0.7 |
| C ₄ H ₁₀ | 13.31 | 18.51 | 15.16 | 10.68 | 15.16 | 11.55 | 10.29 | 10.69 | 9.09 | 13.74 | 12.00 ± 0.3 |
| C ₅ H ₁₂ | 15.63 | 22.05 | | 12.77 | 18.80 | | 11.09 | 13.58 | 10.28 | 16.08 | 15.7 |
| C ₆ H ₁₄ | 18.11 | 24.36 | | 14.98 | 20.04 | 16.98 | 13.58 | 14.56 | 13.16 | 18.57 | |
| C ₇ H ₁₆ | 20.48 | 24.36 | | 17.11 | 24.21 | | 15.20 | 16.12 | | 20.97 | |
| C ₈ H ₁₈ | 22.80 | 31.29 | | 19.20 | 28.34 | | 16.79 | 16.17 | 16.26 | 23.30 | |
| Naphthenes | | | | | | | | | | | |
| C ₃ H ₆ | 10.48 | 7.41 | | 8.14 | | | 8.24 | | | 11.14 | |
| C ₄ H ₈ | 13.49 | 7.66 ^c | | 10.84 | | | 10.30 | | | 14.25 | |
| C ₅ H ₁₀ | 15.78 | 8.85 ^c | | 12.90 | | 13.51 ⁰ | 11.87 | | | 16.64 | |
| C ₆ H ₁₂ | 18.62 | 10.25 ⁰ | | 15.45 | | | 13.81 | | | 19.59 | |
| Olefins | | | | | | | | | | | |
| C ₂ H ₄ | 5.72 | | | 3.86 | | | 4.98 | | | 6.20 | |
| C ₂ H ₂ | 6.90 | | | 4.92 | | | 5.79 | | | 7.41 | |
| C ₃ H ₆ | 9.98 | | | 7.68 | | | 7.89 | | | 10.61 | |
| C ₄ H ₆ | 10.72 | | | 8.35 | | | 8.80 | | | 10.06 | |
| C ₆ H ₆ | 14.23 | | | 11.50 | | | 10.80 | | | 11.38 | |
| C ₆ H ₂ | 14.83 | | | 12.04 | | | 11.21 | | | 15.64 | |
| Aromatics | | | | | | | | | | | |
| C ₆ H ₆ | 16.06 | 19.81 | | 13.15 | | 13.82 | 12.06 | | | 16.93 | |
| C ₆ H ₅ CH ₃ | 18.39 | 11.99 | | 15.24 | | | 13.65 | | | 19.34 | |
| <i>o</i> -C ₆ H ₅ (CH ₃) ₂ | 21.08 | 4.56 | | 17.57 | | | 15.43 | | 21.7 ^f | 22.02 | |
| <i>m</i> -C ₆ H ₅ (CH ₃) ₂ | 21.19 | 4.14 | | 17.66 | | | 15.50 | | 20.2 ^f | 22.14 | |
| <i>p</i> -C ₆ H ₅ (CH ₃) ₂ | 22.09 | 4.31 | | 17.76 | | | 15.57 | | 18.3 ^f | 22.25 | |
| C ₆ H ₅ C ₂ H ₅ | 20.09 | | | 18.57 | | | 16.19 | | 20.4 ^f | 23.19 | |

^a Reference 7. ^b Reference 8. ^c Reference 8. ^d Reference 9. ^e Reference 5. ^f Reference 6. ^g PW: present work.

Table 2. Polarizabilities (α_M), Heats of Adsorption (ΔH), and Activation Energies (E) of Normal Paraffins Cracking on ZSM-5

| carbon number | chain length (Å) | $\alpha_M (10^{-25} \text{ cm}^3)$ | | $-\Delta H (\text{ k cal/mol})$ | | $En^* (\text{ k cal/mol})$ | |
|---------------|---------------------------------|------------------------------------|--------------------|---------------------------------|--------------------|----------------------------|--------------------|
| | | theo ^a | exptl ^b | theo ^a | exptl ^c | theo ^a | exptl ^d |
| 1. | CH ₄ | 4.1 | 25.0 | 25.9 | 5.26 | 34.71 | |
| 2. | C ₂ H ₆ | 5.26 | 42.0 | 44.3 | 7.65 | 32.32 | |
| 3. | C ₃ H ₈ | 6.52 | 59.0 | 63.6 | 10.04 | 29.93 | |
| 4. | C ₄ H ₁₀ | 7.78 | 75.0 | 82.0 | 12.43 | 27.54 | 34 |
| 5. | C ₅ H ₁₂ | 9.04 | 92.0 | 99.9 | 14.82 | 25.15 | |
| 6. | C ₆ H ₁₄ | 10.30 | 100.0 | 118.9 | 17.21 | 22.76 | 30 |
| 7. | C ₇ H ₁₆ | 11.56 | 130.0 | 137.0 | 19.60 | 20.37 | |
| 8. | C ₈ H ₁₈ | 12.82 | 140.0 | 155.0 | 21.99 | 17.98 | 22 |
| 9. | C ₉ H ₂₀ | 14.08 | 160.0 | 173.6 | 24.38 | 15.59 | 20 |
| 10. | C ₁₀ H ₂₂ | 15.34 | 170.0 | 191.0 | 26.77 | 13.2 | 16 |
| 11. | C ₁₁ H ₂₄ | 16.60 | 190.0 | 210.3 | 29.16 | 10.81 | |
| 12. | C ₁₂ H ₂₆ | 17.86 | 210.0 | 227.5 | 31.55 | 8.42 | |
| 13. | C ₁₃ H ₂₈ | 19.12 | 230.0 | | 33.94 | 6.03 | |
| 14. | C ₁₄ H ₃₀ | 20.38 | 240.0 | | 36.33 | 3.64 | |
| 15. | C ₁₅ H ₃₂ | 21.64 | 260.0 | | 38.72 | 1.25 | |
| 16. | C ₁₆ H ₃₄ | 22.90 | 280.0 | | 41.11 | -1.14 | |
| 17. | C ₁₇ H ₃₆ | 24.16 | 290.0 | | 43.50 | -3.92 | |
| 18. | C ₁₈ H ₃₈ | 25.42 | 310.0 | | 45.89 | -5.92 | |
| 19. | C ₁₉ H ₄₀ | 26.68 | 330.0 | | 48.28 | -8.31 | |
| 20. | C ₂₀ H ₄₂ | 27.94 | 340.0 | | 50.67 | -10.70 | |
| 21. | C ₂₁ H ₄₄ | 29.20 | 360.0 | | 53.06 | -13.09 | |
| 22. | C ₂₂ H ₄₆ | 30.46 | 380.0 | | 55.45 | -15.45 | |
| 23. | C ₂₃ H ₄₈ | 31.46 | 390.0 | | 57.84 | -17.87 | |
| 24. | C ₂₄ H ₅₀ | 32.98 | 410.0 | | 60.23 | -20.26 | |
| 25. | C ₂₅ H ₅₂ | 34.24 | 430.0 | | 62.62 | -22.65 | |

^a Theo: theoretical values from present study. ^b Experimental values of polarizabilities: Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M., Dielectric Properties and Molecular Behavior; vannons trand: London, 1969; p 192. ^c Reference 51. ^d Apparent activation energy quoted by Haag. Reference 49. ^e Stach H., Fiedler K., Janchen, J. *Pure Appl. Chem.* 65, 2193, 1993.

Thus, the true or intrinsic activation energy, E_0 , is the difference between the observed activation energy En^* and the sorption enthalpy ΔH . Contrary to the intrinsic activation energy, E_0 , the apparent activation energy, En^* , also relates

with the number of carbon atoms (n) and heat of adsorption via the relation of the form³⁶ $En^* = En + \Delta Hn$. An analogous equation in terms of average polarizabilities of hydrocarbons reads $En^* = En - 0.1\alpha_M - 4$, here. α_M is

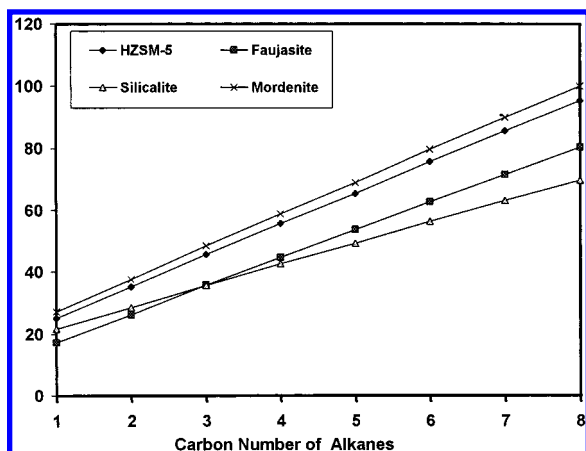


Figure 3. Trends of heats of adsorption of *n*-alkane of different zeolite surfaces as a function of their carbon number.

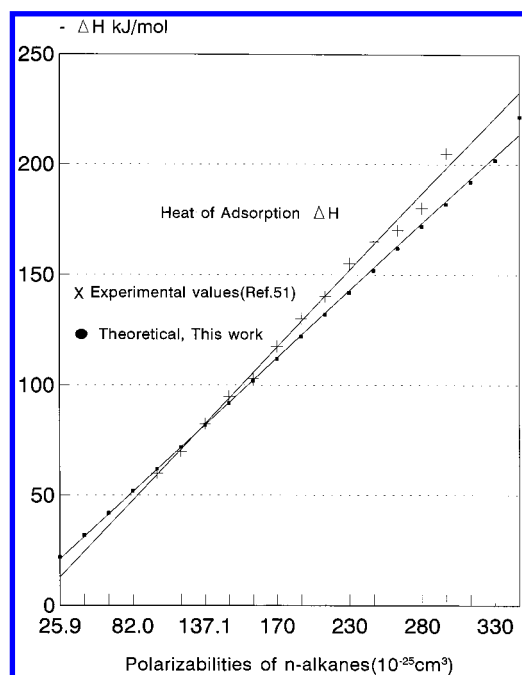


Figure 4. Heat of adsorption *n*-alkanes. (C_1 – C_{20}) versus polarizabilities on HZSM5.

the average polarizabilities of the *n*-alkanes, and the intrinsic activation energy E_n is the difference between observed activation energy E_n^* and sorption enthalpy ΔH . In Figure 5, the apparent activation energies of cracking reaction for $n = 3$ – 25 have been plotted from the literature data. The value of E_n^* (kcal/mol) = $E_n + \Delta H_n = 36 - 0.1\alpha_M$. Here ΔH_n stands for the heat of adsorption of hydrocarbon from carbon number $n = 5$ to $n = 20$. At the value of $n = 16$, the value of E_n^* will turn from positive to negative, and hence the cracking reaction rate will turn with temperature. For the cracking of normal alkanes over ZSM-5, a linear decline of the activation energy of reaction with n was reported by Bizrech and Gates,⁴² Hopkins,⁴³ Richards and Rees,⁴⁴ and Haag.⁴⁹ At a high value of n , the activation energy will turn negative. Indeed, Smith⁴⁰ found experimentally the negative value of apparent activation energy. This requires special attention to explain. According to Larsen⁴⁵ the selective energy transfer from the zeolites to the reactants (mode selectivity) has been demonstrated in reactions catalyzed by zeolites. The mode selectivity is

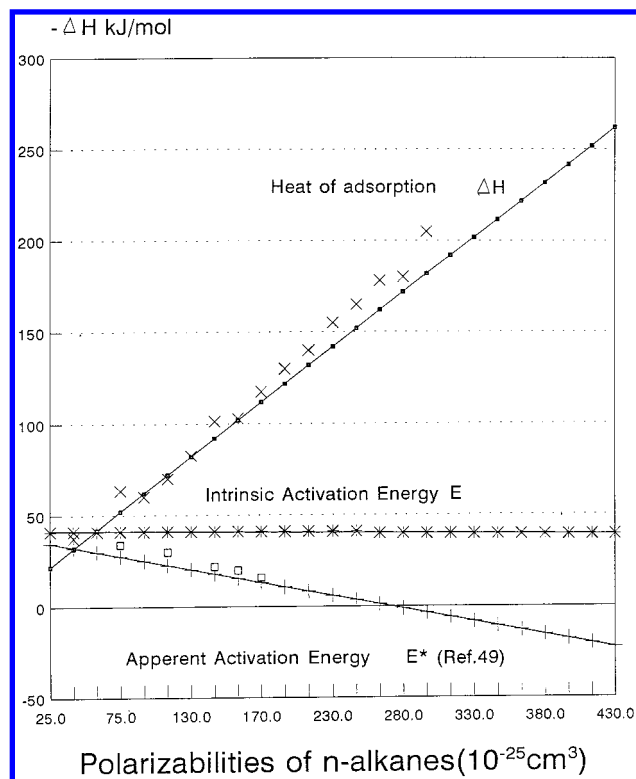


Figure 5. Heats of adsorption, intrinsic apparent activation energies and polarizabilities of *n*-alkanes (C_1 – C_{25}) on HZSM-5.

defined as the “special energy investment into reactants so that the reaction is directed to specific product”. Such considerations had also been the principal basis for the treatments of absolute rates in the RRKM theory.⁴⁶ Larsen⁴⁵ has further argued that the substrate catalyst complex can be regarded as analogous to forced damped oscillator. Under the resonance condition, the more polarizable paraffins with higher chain length (see Table 2) will absorb more energy from the applied field (zeolites) and hence the activation energy will decrease; see Figure 5.

IV. CONCLUSIONS

Using the principle of differential geometry, the curvature of zeolite surfaces, MOR, FAU, ZSM-5, and silicalite, has been established to be $-0.0675/\text{\AA}^2$, $-0.0445/\text{\AA}^2$, $-0.065/\text{\AA}^2$, and $-0.0584/\text{\AA}^2$, respectively using formula 9 and/or by studying the published heats of adsorptions of hydrocarbons. However, the success of the present model will depend on how accurately the average polarizabilities of the hydrocarbon species is determined experimentally by refractive index measurements, light scattering experiment or molar Kerr constant determination or predicted theoretically, and how accurately the surface curvature is defined. It has been found that the same alkane adsorbing on different zeolites surfaces possess different heats of adsorption could be explained on the consideration of the concept of curvature of zeolite surface, polarizabilities of hydrocarbons, and residual atomic polarizability degree of freedom of the zeolite structures. Also the difference in the heats of adsorptions of hydrocarbons with the same carbon number but differing in structure and adsorbing on the same surface could be explained on the basis of the difference in their electronic polarizabilities which is a structure dependent electrical property of hydro-

carbons and curvature of zeolite surface. The significance of decreasing activation energy with increasing polarizability, Figure 5, is that under the thermodynamic equilibrium, the molecule is in resonance⁴⁵ and absorbs energy from the applied field (zeolite). The anomalous decrease in the activation energies of *n*-alkanes cracking after C₁₆⁺, the C-16 effect,⁴⁷ could be explained in terms of the contribution from the internal vibrations of zeolites whose frequencies are in resonance with the skeleton vibrations of hydrocarbons at isocatalytic temperature (a temperature at which the plots of $\ln k$ versus $1/T$ cut the *x*-axis using the Arrhenius equation) and has been described in detail elsewhere.⁴⁸ We also feel that more data on heats of adsorptions especially on aromatics (PNAs), polyenes, and higher naphthenes are needed so that simulation of the cracking pattern of hydrocarbons relevant to FCC feedstock could be generated by understanding their activation pattern.

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