

# Heats of Adsorption in Molecules

**Dr. Anupama Sharma**

Associate Professor, Maya Group of Colleges Dehradun

## ABSTRACT

The number of chemical reactions proceed by the phenomenon of adsorption of organic molecules the heat is liberated which is called the heat of adsorption and this can be calculated by using the mathematical chemistry and Gauss Bonnet Theory differential geometry. When the molecules is absorbed on the interacting surfaces of organic molecules the phenomenon is called adsorption. The physico-chemical properties of organic molecules depends on the nature of catalytic surfaces of organic molecules. The importance of this methods used in the study of bio-chemical reaction and catalytic reaction proceed on the surfaces of organic molecules.

**Keywords:** Adsorption

## INTRODUCTION

- Adsorption is the net accumulation of a chemical species at the interface between a solid phase and an aqueous solution phase, leading to a loss from the solution phase.
- It plays a significant role in catalytic reactions like isomerisation, oligomerisation, alkylation and cracking of hydrocarbons and many more processes like adsorptives separations of isomers<sup>3</sup>.
- The study of adsorption energies (Heats of adsorption  $DH$ ) on such system provides strength of adsorbate surface
- As such adsorption is a surface phenomenon. Most of the study reported so far may be classified into three groups.
- Firstly, those which deal with adsorption of molecules on metal surfaces, secondly the adsorption of hydrocarbons of materials like surfaces of zeolites, clay and hetropoly acids and thirdly those which deal with the adsorption of proteins on solids and are responsible in biochemical reactions<sup>4</sup>.
- bond and thermodynamic driving forces responsible for such processes.

## SURFACE

- Mathematically, a surface is defined as  $Z = f(x,y)$  and its curvature is defined by Gauss Bonnet theorem<sup>6</sup>.
- In catalysis and biochemical reactions like adsorption of protein and hydrocarbons takes place on such surfaces.
- Under suitable conditions these molecules are activated and reach to a transition state and finally adopt a suitable pathway of transformation by desorption.
- This molecular process is terminated after liberating some heat called heat of adsorption ( $DH$ ).
- This could be measured with the help of micro calorimetry or other methods. In order to understand this phenomenon of adsorption, activation and desorption a number of mathematical models have been

proposed soon after the proposal of Langmuir adsorption theory<sup>7</sup>.

- During recent days a number of quantum theoretical methods like Monte Carlo simulation and ab initio methods and applied for complicated system of hydrocarbons as well as amino acid to model the system of interest<sup>8</sup>.
- In this paper we have follow a simple approach for predicting the heat of adsorption taking the case of pentane over two different surfaces ZSM-5 or Silicalite whose most general MFI structure shown in Fig 1-2. ZSM-5 (MFI topology) is a very important zeolite and is widely used as shape- selective catalysts in industry.

## 1. EXPERIMENTAL AND THEORETICAL DETAILS AND METHODS

- The curvature of surfaces of ZSM-5 and silicalite were calculated with the help of Gauss-Bonnet theorem as describe by ANDERSSON.
- The Gauss Bonnet Theorem reads as follows:
- Using the numerical integration of the Weierstrass equation one can easily
- calculate the cartesian coordinates and Gaussian curvatures of the D, P and G surfaces.
- If  $dA$  is the area of a surface element  $S$  and  $dA'$  is the Gauss map  $S^*$  of  $S$ , then :
- Thus  $\iint dA = \iint S^* K ds A' / K$

## 2. HEAT OF ADSORPTION

- Where  $N$  is the bonding electron per molecule which scales very well with the average polarizabilities of hydrocarbons and  $S$  is surface constant. Hence a differential heat of adsorption
- Can be calculated. By assuming that the adsorbate- adsorbent interaction is very clean and the adsorbate-adsorbate interaction is negligible.
- $DH = S N . K_{av}$  10
- Where  $S$  is another interface constant considering the above facts it is worth while to quantify initial heat of adsorption.  $H$  in terms of the curvature of the catalyst surface the delta function polarizability  $\alpha_m$  of the interacting hydrocarbons and surface constant by the relation.
- $DH = \alpha_m . \alpha + \epsilon f$  11
- In a recent work, the study has been extended to hydrocarbons. Having deciphered the values of the heats of adsorption the activation energy  $E$  has been verified by Evans-Polyani method to explain the reaction rates.
- Inside a zeolite molecule should feel an attractive force  $F$
- $F = \text{Constant} . N . K_{av}$  12

## 3. OBSERVATIONS AND RESULTS

- The curvature of ZSM – 5 and silicalite calculated on the basis of differential geometry and Gauss Bonnet theorem has been found to be  $-0.065A$  and  $-0.0584A$
- The heat of adsorption on these two surfaces are found to be 14.82 on ZSM- 5 and 15.15–A. on silicalite surfaces respectively. The experimental values

## 4. DISCUSSION

- The area of surface contained in one unit cell of the dealuminated faujasite structure of unit cell  $a =$

24.20 Å becomes 2261 Å<sup>2</sup> and a tetrahedral saddle 47.11 Å<sup>2</sup>. and the average curvature is:

- $K_{av} = -2/3 \cdot p / 47.11 = -0.0445 \text{ Å}^2$ .
- This equation was now tested by using accurate adsorption heats of hydrocarbons in estimating the surface curvature of mordenite, silicalite, and ZSM-5 that was found to be -0.04, -0.05 and -0.03 Å<sup>2</sup> respectively.
- The heats of adsorption data<sup>8</sup> for paraffins, naphthenes, aromatic, olefins on different zeolites surfaces were computed using the above curvature data and their polarizabilities.
- The data on heats of adsorption shows fair degree of agreement with the experimental values.
- Only the representative data on adsorption and activation energy of n-alkanes ZSM-
- 5 system have been collected and displayed in Fig 3
- The detailed account of adsorption data of hydrocarbons on zeolite surfaces are
- On the Basis these workers (19) Verified the measurement of Stach.ET.AL (13, 19) on the heat of adsorption of hydrocarbons on different Zeolites.
- Considering above observe facts, it is worth to quantify initial heat of adsorption  $DH$  in terms of curvature of zeolite surface =  $K_{av}$ , the delta function polarizability  $\Delta\alpha$  of interacting hydrocarbons.

obtained by Stach, Fiedler and Janchen are 14.35 kilo calorie/mole.

- This value matches very closely with our theoretical results showing the basic soundness of the method adopted.
- Taking the advantage of this calculation, the heats of adsorption for alkanes on mordenite and faujasite has been calculated and displayed in Fig3 available to justify a method of calculation but taking the case of pentane, that absorbs on ZSM -5 and silicalite gives different values of  $DH$  although the value of content is the same meaning thereby the surface quantity curvature plays a significant role in adsorption phenomenon this is the reason why the same hydrocarbon species adsorb on two different surfaces possess different heat of adsorption and hence different rates of chemical reaction.
- The heats of adsorption of n-alkanes are proportional to the curvature of ZSM-5 surface and vary as the product of surface curvature and the electric polarizabilities of n-paraffins.
- This observation is in line with similar increase with carbon number or chain length with a difference that our treatment is based on the cooperative effect between adsorbate and substrate and explains clearly why heats of adsorption of the same alkane interacting with different zeolites should possess different  $DH$  values

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