

# CALCULATION OF NITROGEN HEAT ADSORPTION ON VARIOUS CATALYSTS USING BET-CONSTANT (BET-C) DATA

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## ABSTRACT

*BET-C (Brunauer-Emmett-Teller-Constant) was used to calculate the heat of adsorption ( $\Delta H_{ads}$ ) of nitrogen gas on the various catalysts. The well-known Brunauer-Emmett-Teller (B.E.T.) equation is used primarily to determine the surface area from the physical adsorption of a gas on a solid surface. Surface area of catalysts was determined by using surface area analyzer (NOVA 1000).*

*The BET-C included in the data is usually neglected or is not taken into account. However, by using the basic principles of the adsorption theory fitted with the functions based on the BET adsorption model, the important data of BET-C can be shown in this study. The value of the  $\Delta H_{ads}$  ( $N_2$ ) for zeolite, H-zeolite, Pt/zeolite, Pt-Pd/zeolite, and Pt-Ce/zeolite calculated from the equation derived from BET-C are -6.43, -6.52, -8.78, -8.69, -9.71 and -9.52 kJ/mol, respectively.*

*Key words: BET, adsorption, catalyst, surface area*

## I. INTRODUCTION

Gas adsorption is practical consequence to chemists in many ways. The phenomenon of surface adsorption has been used to modify the rates of product yields of chemical reactions through heterogeneous catalysis<sup>(1)</sup>. A good performance catalyst have a large surface area, bind the reactants quickly and effectively, stabilize the activated complex, and release the products of the reaction<sup>(2)</sup>. Thus, the attraction of various molecules on the surface is extremely important properties of potential catalytic materials. This study will investigate the adsorption of  $N_2$  at cryogenic temperatures on several catalysts and a high area support such as zeolite. The BET-C information will be used to estimate the heat of adsorption of  $N_2$  gas. Most methods are based on the isothermal adsorption of nitrogen. Either a single point or multipoint, adsorption method is used to calculate the surface area. BET equation is then used to calculate the

total surface area. It is also used as a quality control during catalyst performance testing<sup>(3,4)</sup>. These attributes are measured by the use of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures (P/Po) ranging from 0.05-1.0. The large uptake of nitrogen at low P/Po indicates of filling of the micropores (< 20 Angstrom) in the catalyst. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface of the catalyst, and the concave upward portion of the curve represents of filling of mesopores (20 - 500 Angstrom) and macro pores (>500 Angstrom). An entire isotherm is needed to calculate the pore size distribution of the catalyst. However, for a surface area evaluation, data in the relative pressure range of 0.05-0.30 are generally used. Different analyses can be applied to these data to develop specific information. For example, application of the surface area, average pore radius and pore volume provide

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information about of the catalyst quality, whereas, in this study, the BET-C is used to determine the strength of the interaction between adsorbate (nitrogen) and catalysts (zeolite based catalysts).

The interaction of a molecule with a given surface will also be dependent upon the presence of any existing adsorbed species, whether these are surface impurities or simply pre-adsorbed molecules of the same type. The energy of adsorption is *negative*, and since it corresponds to the energy *change* upon adsorption it is better represented as  $\Delta E(\text{ads})$  or  $\Delta E_{\text{ads}}$  associated with the enthalpy of adsorption,  $\Delta H(\text{ads})$ . There is of course a significant barrier to the reverse, desorption process in the diagram below represents the activation energy for desorption<sup>(5)</sup> (Figure 1).

Clearly in this particular case, the magnitudes of the energy of adsorption and the activation energy for desorption can also be represented as follows:

$$E_a^{\text{des}} = \Delta E(\text{ads}) \quad \text{or} \quad E_a^{\text{des}} \sim -\Delta H(\text{ads})$$

A qualitative distinction is usually made between chemisorption and physisorption, in terms of the relative binding strengths and mechanisms. In chemisorption, a strong 'chemical bond' is formed between the adsorbate and the catalysts. In this case, the adsorption energy,  $E_a$ , of the adsorbed atom is likely to be a good fraction of the sublimation energy of the substrate, and it could be more<sup>(6)</sup>. Physisorption is often described as implying that no chemical interaction is present. This can't really be true, because if there were no attractive interaction, then the atom would not stay on the surface for any measurable time and

it would simply bounce back into the vapor. A better distinction is that in physisorption, the energy of interaction is largely due to the van der Waals force<sup>(7)</sup>. This force is due to fluctuating dipole (and higher order) moments on the interacting adsorbate and substrate, and is present between closed-shell systems. Adsorbate is a substance adhered to a surface (the adsorbent). The quantity of adsorbate present on a surface depends on several factors including: adsorbent type, adsorbate type, size, concentration, temperature and pressure. Some adsorbate is listed in Table 1 and the corresponding cross-sectional area which can be used for determining solid surface area<sup>(8)</sup>.

Surface area of a catalyst can be measured by either a multipoint or single point technique. In either the single point or multipoint method, the isotherm points are transformed with the BET equation:

$$\frac{1}{W[(P_o/P) - 1]} = \frac{1}{W_m C} + \frac{(C-1)}{W_m C} \frac{P}{P_o}$$

Where, W is the weight of nitrogen adsorbed at a given  $P/P_o$ , and  $W_m$  the weight of gas to give monolayer coverage and C, a constant that is related to the heat of adsorption.

## II. EXPERIMENTAL

The zeolite based catalysts used as adsorbents in this investigation such as zeolite, H-zeolite, Pt/Zeolite, Pd/Zeolite, Pt-Pd/Zeolite, Pt-Ce/Zeolite. The zeolite used was activated Indonesian natural zeolite. A portion was then exchanged with ammonium nitrate and it was heated up to produce H-zeolite. The metal was added to the support by impregnation method. The zeolite was dipped or immersed in a solution which contains noble metals. The noble metals will adhere to the surface of the support. After the impregnation, solvent was then evaporated at boiling temperature, the catalyst was dried in the oven overnight and thereafter the catalyst was activated under hydrogen stream of 10 mL/min for 2 hours. In the solution used for the impregnation, platinum has a valence of 4. The  $\text{Pt}^{\text{IV}}$  compounds that used for impregnation was hexachloroplatinic(IV) acid ( $\text{H}_2 \text{Pt}^{\text{IV}} \text{Cl}_6$ ).

Prior to surface area and BET-C determination, the catalyst samples were evacuated by degassing at 250°C for 4 hours. All data were collected on the same instrument and were obtained at nitrogen  $P/P_o$  values of 0.08, 0.11, 0.14, 0.17 and 0.20.

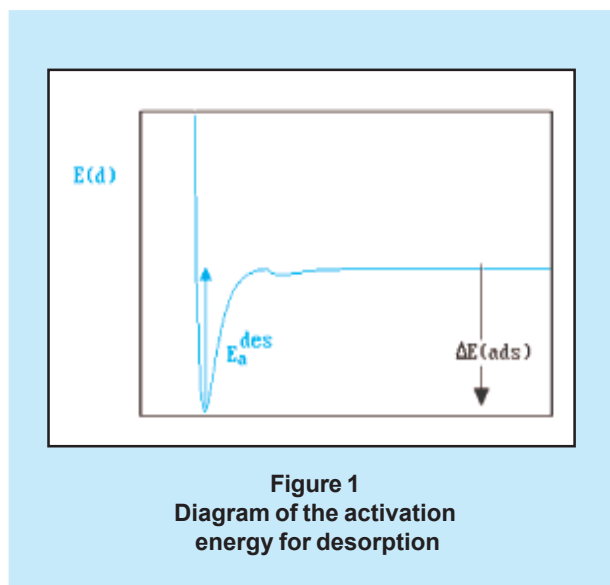


Figure 1  
 Diagram of the activation  
 energy for desorption

### III. RESULT AND DISCUSSION

#### Surface area and BET-C data:

The adsorbents used for this experiment were zeolite, H-zeolite, Pt/Zeolite, Pd/Zeolite, Pt-Pd/Zeolite, Pt-Ce/Zeolite. The N<sub>2</sub> was used as adsorbate. The results of determinations of the BET-C and surface area of zeolite-based adsorbents are summarized in Table 2.

As seen in Table 2 that the surface area and the BET-C are depending on the present of metal in the zeolite based adsorbents. Bimetal adsorbent demonstrates a significantly higher BET-C than the zeolite itself as well as monometal/zeolite adsorbent. The results indicate that surface area and BET-C data increase with the increase of the metal content on the zeolite based adsorbent. This phenomenon proves that the adsorption of nitrogen by adsorbent is mainly caused by the metal-nitrogen interaction.

#### Calculation of heat adsorption:

Considering adsorption process, the surface covered in monolayer, bilayers, and so on. The first layer of the adsorption,



A = adsorbate S = active sites AS = Adsorbate adsorbed on the active sites

The relation between adsorption standard free energy changes and the adsorption equilibrium constant of this process is:

$$\Delta G_{adsorption}^{\circ} = -RT \ln K$$

$$K = e^{-\left(\Delta G_{adsorption}^{\circ} / RT\right)}$$

$$K = e^{\left(\Delta G_{desorption}^{\circ} / RT\right)}$$

The second and further layer of the adsorption, the process is similar to condensation-evaporation.



When, K<sub>1</sub> is the equilibrium constant for vapor

**Table 1**  
 Lists of some adsorbate cross-sectional areas

No.	Adsorbate	Area (Å)	ΔH <sub>vap</sub> (kJ/mole)
1.	Nitrogen	16.2	2.79
2.	Ammonia	14.6	23.35
3.	Benzene	40.0	42.90
4.	Carbon dioxide	19.5	25.13
5.	Carbon monoxide	16.3	6.02
6.	Ethane	20.5	7.82
7.	n-Butane	46.9	21.00
8.	n-Hexane	51.0	28.96
9.	Oxygen	14.1	3.41
10	Water	10.8	40.65

**Table 2**  
 Surface area and BET-C data of zeolite-based adsorbents

No.	Catalyst/adsorbent	BET-C	Surface Area (m <sup>2</sup> /g)
1.	Zeolite	85.82	47.31
2.	H-zeolite	92.05	98.66
3.	Pt/Zeolite	1426.27	129.14
4.	Pd/Zeolite	1114.53	108.56
5.	Pt-Pd/Zeolite	4376.03	109.38
6.	Pt-Ce/Zeolite	3527.99	111.28

condensation, the relation between condensation standard free energy changes and the condensation-evaporation equilibrium constant is:

$$\Delta G_{condensation}^{\circ} = -RT \ln K_1$$

$$K_1 = e^{-\left(\Delta G_{condensation}^{\circ} / RT\right)}$$

$$K_1 = e^{\left(\Delta G_{vaporization}^{\circ} / RT\right)}$$

Introducing a new constant used as a BET constant, C, the ratio between equilibrium constant of first layer adsorption to the second layer,

$$C = \frac{K}{K_1}$$

$$C = \frac{e^{(\Delta G_{adsorption}^o / RT)}}{e^{(\Delta G_{vaporization}^o / RT)}}$$

$$C = e^{(\Delta G_{adsorption}^o - \Delta G_{vaporization}^o) / RT}$$

$$\Delta G_{adsorption}^o = \Delta H_{adsorption}^o - T\Delta S_{adsorption}^o$$

$$\Delta G_{condensation}^o = \Delta H_{condensation}^o - T\Delta S_{condensation}^o$$

The entropies of desorption and vaporization are similar,

$$\Delta S_{condensation}^o = \Delta S_{adsorption}^o$$

and

$$\Delta H_{condensation}^o = \Delta H_{adsorption}^o \text{ or } \Delta H_{vaporization}^o = \Delta H_{desorption}^o$$

$$C = e^{(\Delta H_{adsorption}^o + \Delta H_{vaporization}^o) / RT}$$

$$RT \ln C = \Delta H_{vaporization}^o - \Delta H_{adsorption}^o$$

$$\Delta H_{adsorption}^o = \Delta H_{vaporization}^o - RT \ln C$$

By knowing BET-C and the standard enthalpy of vaporization ( $\Delta H_{ads}^o$  of  $N_2$ ) at boiling temperature, the enthalpy of adsorption can be calculated. The results are listed in Table 3.

Using the basic principles of the adsorption theory fitted with the functions based on the BET adsorption model, the important data of BET-C can be shown. The value for the  $\Delta H_{ads}$  ( $N_2$ ) for

zeolite, H-zeolite, Pt/zeolite, Pt-Pd/zeolite, and Pt-Ce/zeolite calculated from the equation derived from BET-C are -3.67, -3.73, -5.99, -5.79, -6.92 and -6.75 kJ/mol respectively. There is a slightly difference values of the  $\Delta H_{ads}$  ( $N_2$ ) among the catalysts because of its calculation in thermal analysis. The value for the  $\Delta H_{ads}$  ( $N_2$ ) for Pt/zeolite is  $-5.61 \pm 0.14$  kJ/mol and the  $\Delta H_{ads}$  ( $N_2$ ) for Pd/zeolite is  $-5.58 \pm 0.26$  kJ/mol.

The data in Table 3 were calculated under the following assumptions: (1) Adsorbed molecules were always stay on top of the site, (2) Energy of adsorption was same for any layer other than the first layer, (3) A new layer could be started before another layer was finished. With these assumptions, there is a slight difference in the adsorption and desorption runs. It is due to the differences of observation in the adsorption and desorption isotherms. For alumina there is not much evidence of this case, but the path is more pronounced in the silica isotherm.

An alternative method to approach this adsorption problem is to use the Langmuir theory. The Langmuir theory differs from the BET theory slightly. The assumptions that is made in the Langmuir theory as follows: (a) Adsorption cannot proceed beyond monolayer coverage; (b) All sites are equivalent and the surface is uniform; and (c) The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites. The Langmuir theory holds under low pressures whereas the BET theory may fail. The problem with the Langmuir theory is that at high pressures, there may be more than just monolayer coverage. In this investigation, heat of adsorption calculation is only based on the BET theory.

#### IV. CONCLUSION

The results obtained in this investigation showing that surface area measurements based on nitrogen adsorption is unique and useful for heat of adsorption calculation. This investigation shows that

**Table 3**  
**Heat of adsorption of nitrogen on adsorbents**

No.	Catalyst/ adsorbent	BET-C	$\Delta H_{ads}^o$ (kJ/mole) at 90.33K
1.	Zeolite	85.81	3.67
2.	H-zeolite	92.05	3.73
3.	Pt/Zeolite	1426.27	5.99
4.	Pd/Zeolite	1114.53	5.79
5.	Pt-Pd/Zeolite	4376.03	6.92
6.	Pt-Ce/Zeolite	3527.99	6.75

the reason of why the BET-C is put to practical use in every time for surface area measurements.

Gas adsorption has been studied theoretically as the simplest of the resulting theories to provide the insight needed for most applications. It has been investigated such treatments that attributed to Brunauer, Emmett and Teller (BET) and apply their equations to our experimental data. The adsorption of N<sub>2</sub> at cryogenic temperatures is conducted on common high area catalysts. This information was then used to examine the simple adsorption theory and estimate the heat of adsorption of N<sub>2</sub>.

The BET constant can be used to determine the heat of adsorption between the nitrogen as an adsorbate and zeolite based catalysts. The value for the  $\Delta H_{\text{ads}}(\text{N}_2)$  for zeolite, H-zeolite, Pt/zeolite, Pt-Pd/zeolite, and Pt-Ce/zeolite calculated from the equation derived from BET-C are -3.67, -3.73, -5.99, -5.79, -6.92 and -6.75 kJ/mol respectively.

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