

吸附热

摘要:

吸附热是表征吸附类型和不均匀度的的一个很重要的性质。它提供了在特定化学反应下的催化剂的活性信息。在催化剂的表面, 不仅仅有复杂的物理结构, 还展现出许多随吸附能量分布的吸附位。当固体表面暴露在吸附质中, 具有最高吸附热的大部分能量位就会先被覆盖, 最后被覆盖的吸附位的吸附热最低。不均匀性可能会导致吸附热随覆盖度的改变而改变。吸附热可由气体吸附法测定。本文测试了 Y 型分子筛的 NH_3 化学吸附, 并对结果进行了一系列的讨论。

✓ ↩ Application Note -- 55

Heat of Adsorption

Instrument Type: ✓ 2010

Technique: ✓ Physisorption

Introduction

The heat of adsorption is an important property for characterization of the type of sorption and of the degree of heterogeneity. It provides information about catalyst activity toward certain chemical reaction conditions. The surface of a catalyst not only has a complex physical texture, but also exhibits sorption sites having a distribution of sorption energies. When the solid surface is exposed to an adsorbate, the most energetic sites with the highest heats of sorption will be covered first. The last sites to be covered reflect the lowest heats of sorption. The result of heterogeneity is a heat of sorption which may vary with fractional coverage. Heat of sorption can be determined by a gas sorption method. The isosteric heat of sorption can be calculated as a function of volume of gas adsorbed, utilizing the Clausius-Clapeyron equation:

$$\left(\frac{\delta \ln P}{\delta T} \right)_{\theta} = - \frac{q_{st}}{RT^2} \quad (1)$$

where

P = equilibrium pressure of adsorbate (Torr) T = analysis temp (K) θ = degree of coverage defined as volume adsorbed divided by the specific surface area of the adsorbent R = gas constant (0.00831 KJ/mol K) q_{st} = isosteric heat of sorption (KJ/mol)

Integration of the above equation leads to

$$\ln P = - \frac{q_{st}}{R} \frac{1}{T} + C \quad (2)$$

where C is a constant.

Thus, P vs. 1/T gives a straight line. The isosteric heat of sorption can be obtained from the slope.

Experimental

NH₃ chemisorption was performed on zeolite Y. Five samples were pretreated simultaneously and then analyzed one by one at different temperatures. Samples were calcined at 500 °C for 30 minutes under a flow of dry air, followed by 60 minutes evacuation at analysis temperature under a vacuum of 8×10^{-5} mmHg. NH₃ chemisorptions were performed at 100 °C, 175 °C, 300 °C, 400 °C, and 500 °C, respectively. With the sample tube closed, NH₃ was introduced into the manifold system and was equilibrated for 10 seconds. Then the sample, at analysis temperature, was exposed to the gas. A 10-second equilibration time, which took 100 pressure readings spaced 10 seconds apart, was used. The rate of change of pressure from the first to the last pressure point was computed. If the pressure change was not in the specified range, pressure readings were taken automatically every 10 seconds until equilibrium was achieved. Eight pressure points were used for each sample, ranging from 0.5 Torr to 30 Torr. The equilibrium gas volume (including strong and weak chemisorption) chemisorbed for each pressure was recorded. The whole process was completely automated using the described analysis procedure.

Results and Discussion

The general steps to obtain heats of sorption as a function of coverage are as follows:

1. Obtain adsorption isotherms at different analysis temperatures.
2. Obtain isobars from the isotherms.
3. Calculate heat of sorption at constant coverage using equation 2.

Figure 1 shows the NH₃ adsorption isotherms at different temperatures. The big difference in

adsorption volume between 100 °C and 175 °C indicates that weak adsorption, or physisorption, may happen at lower temperatures.

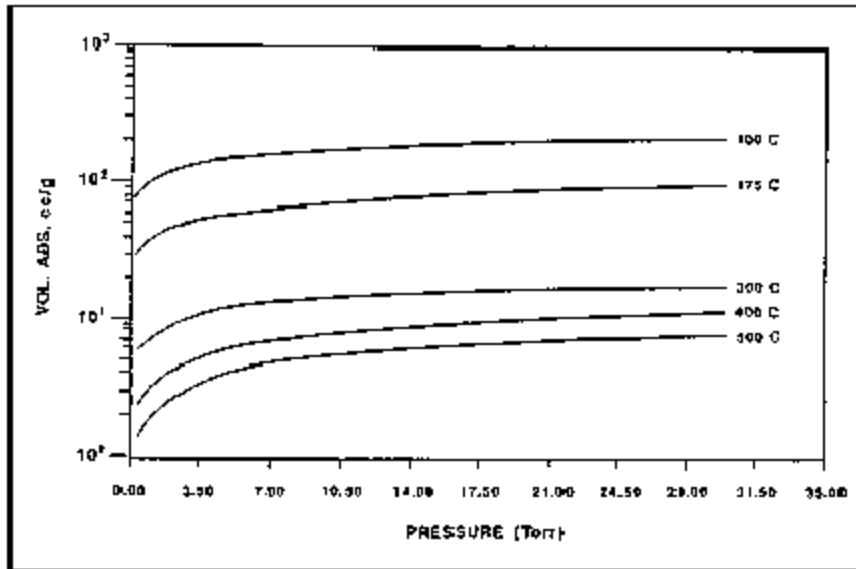


Figure 1. Adsorption Isotherms; Volume of Gas Adsorbed (cc/g STP) as Function of Partial Pressure (Torr)

The volume adsorbed corresponding to constant pressure and different temperatures can be obtained from Figure 1. The adsorption isobar plot (Figure 2) shows this volume of gas adsorbed vs. analysis temperature.

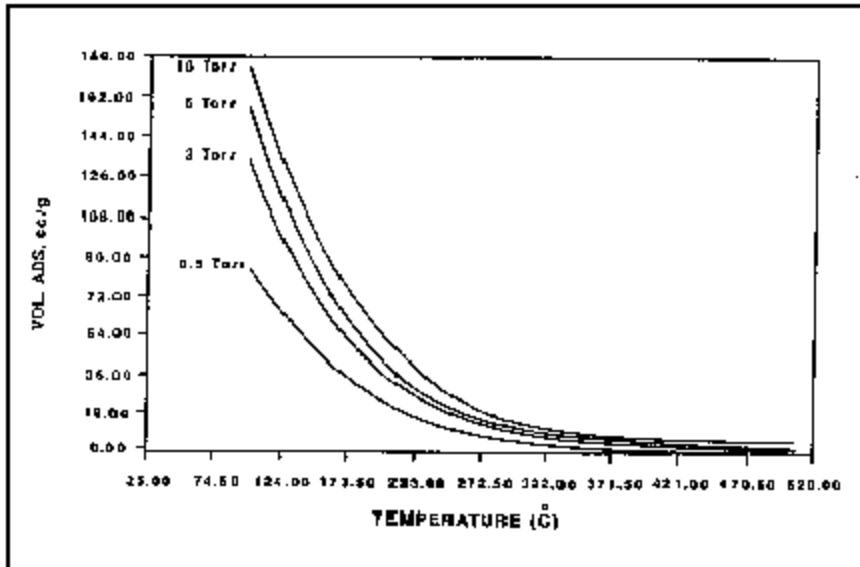


Figure 2. Adsorption Isobars; Volume of Gas Adsorbed (cc/g STP) as Function of Temperature (C)

Pressures and temperatures corresponding to a constant adsorption volume can be obtained from Figure 2. The heat of sorption corresponding to that volume then can be calculated by using equation 2. The volume of gas adsorbed is divided by the specific surface area of the sample to obtain the degree of coverage. This procedure is repeated for different adsorbed volume. Thus, the isosteric heat of adsorption as a function of degree of coverage can be obtained. This final result is plotted in Figure 3.

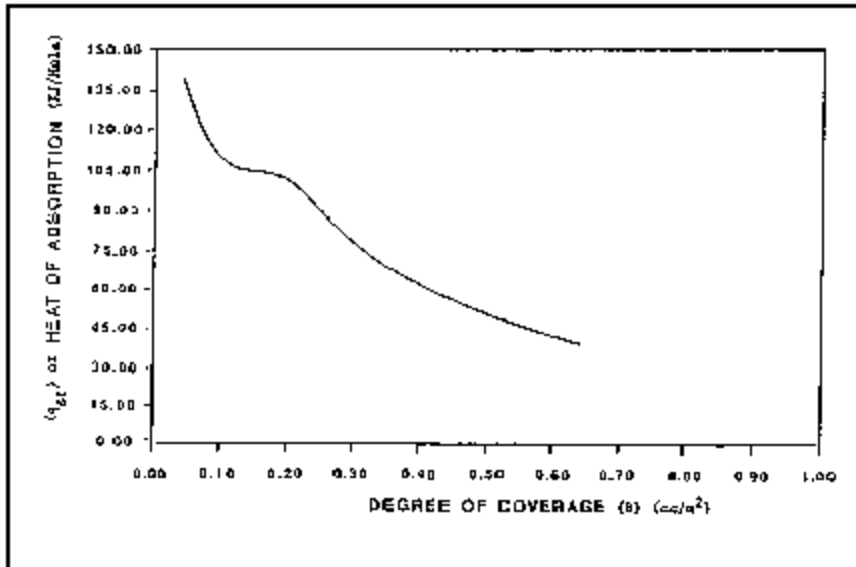


Figure 3. Heat of Adsorption q_{st} as Function of Degree of Coverage

Figure 3 shows the great surface heterogeneity for this sample. At very low coverage the initial heat of sorption is very high, attributable to a few highly active sites. The heat of adsorption drops significantly with the increase of coverage. After the degree of coverage is above 0.5, most of the sorption corresponds to physisorption.

Conclusion

The heat of adsorption is an indication of how strongly the gas is retained by the active sites of the solid. It provides an estimation of the activity of the catalyst toward certain reaction as well as the temperature at which the reaction can occur properly. It is obvious that the first portion of gas, which is adsorbed by the most active sites, reflects the highest heat of adsorption. As the amount of the adsorbate increases over the solid, other sites (including the weakest ones) begin to adsorb. This effect reflects the heterogeneity of the surface by showing the variability of the heat of adsorption as the degree of coverage increases (Figure 3).