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The Science and Technology of Small Particles™

AutoChem II 2920

TECHNIQUE Temperature-Programmed Desorption (TPD)

Temperature-Programmed Desorption (TPD) analyses determine the number, type, and strength of active sites available on the surface of a catalyst from measurements of the amounts of gas desorbed at various temperatures.

After the sample has been outgassed, reduced, or otherwise prepared, a steady stream of analysis gas flows through the sample bed and reacts with the active sites. Programmed desorption begins by raising the temperature linearly with time while a steady stream of inert carrier gas flows through the sample.

At a certain temperature, the thermal energy overcomes the activation energy; therefore, the bond between the adsorbate and adsorbent breaks and the adsorbed species is liberated from the surface and swept away by the carrier gas. If different active metals are present, the chemical bond between the adsorbed molecule and each metal type will likely be of different energy. Therefore the molecules adsorbed on each active metal will require a different thermal energy level to break the bond and desorb, resulting in distinct peaks on the plot of the TCD output signal vs. temperature.

The differential thermal conductivity measured by the detector at any moment is proportional to the instantaneous molecular concentration of desorbed molecules. The volume of the desorbed species obtained from integration of the peak, combined with the stoichiometry factor, yields the number of active sites. Multiple peaks, when they occur, indicate distinct energy differences in active site energies. The combination of high resolution in the AutoChem II 2920 analysis system and its peak separation and integration capabilities allows calculation of the number of sites corresponding to each energy peak.

With the AutoChem II 2920, one also can quantify the energy of desorption associated with a desorption peak. This requires that at least two, but preferably three or more, TPD chromatograms be collected at different heating ramp rates. The derivation of the working equation is presented in a straightforward manner by White (White, M.G., Heterogeneous Catalysis, Prentice Hall, 1990). The equation, rearranged into linear form, permits the energy of desorption to be calculated from the slope term.

A set of reports from the AutoChem II 2920 illustrating energy of desorption determinations is presented in Figure 1. The first illustration (Figure 1a) is a composite plot of ammonia desorption from ZSM-5 at several heating rates. Figure 1b shows the heat of desorption plot from the linear form of the equation discussed above. A regression line is calculated from the data points and the slope of this line is used to determine the heat of desorption.

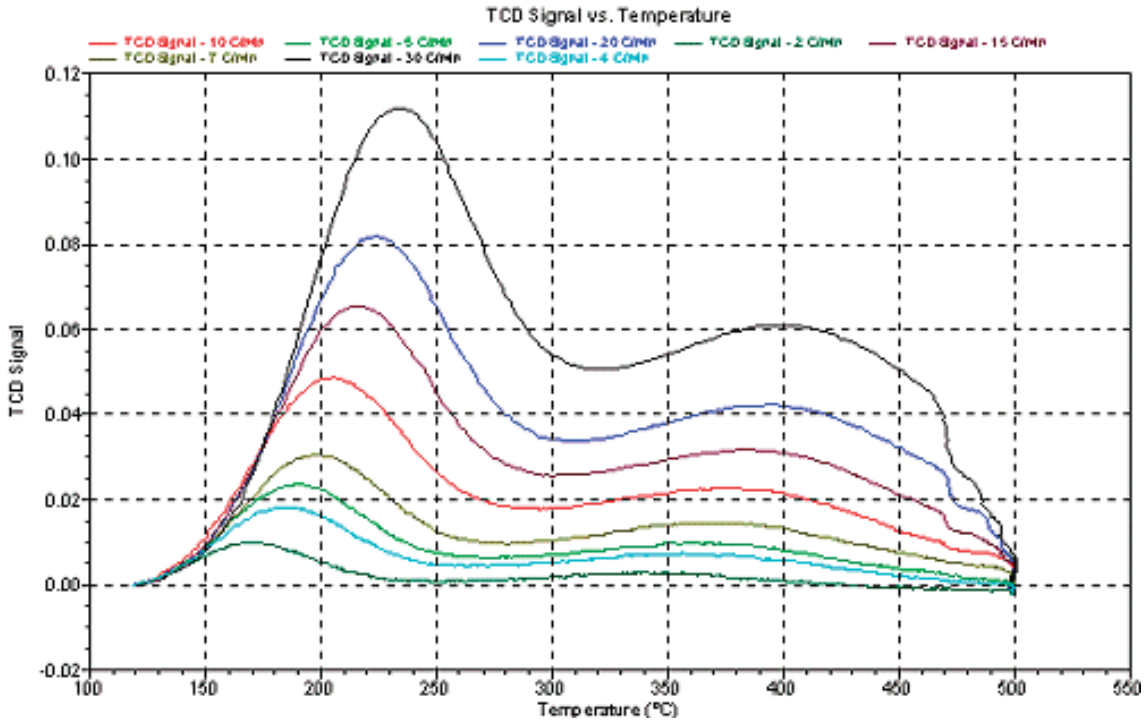

Figure 1a. A set of Temperature-Programmed Desorption profiles from three separate TPD analyses of ammonia on ZSM-5. Each analysis was performed using a different linear heating rate. The AutoChem II 2920 peak editor allows multiple experiments to be plotted on one grid.

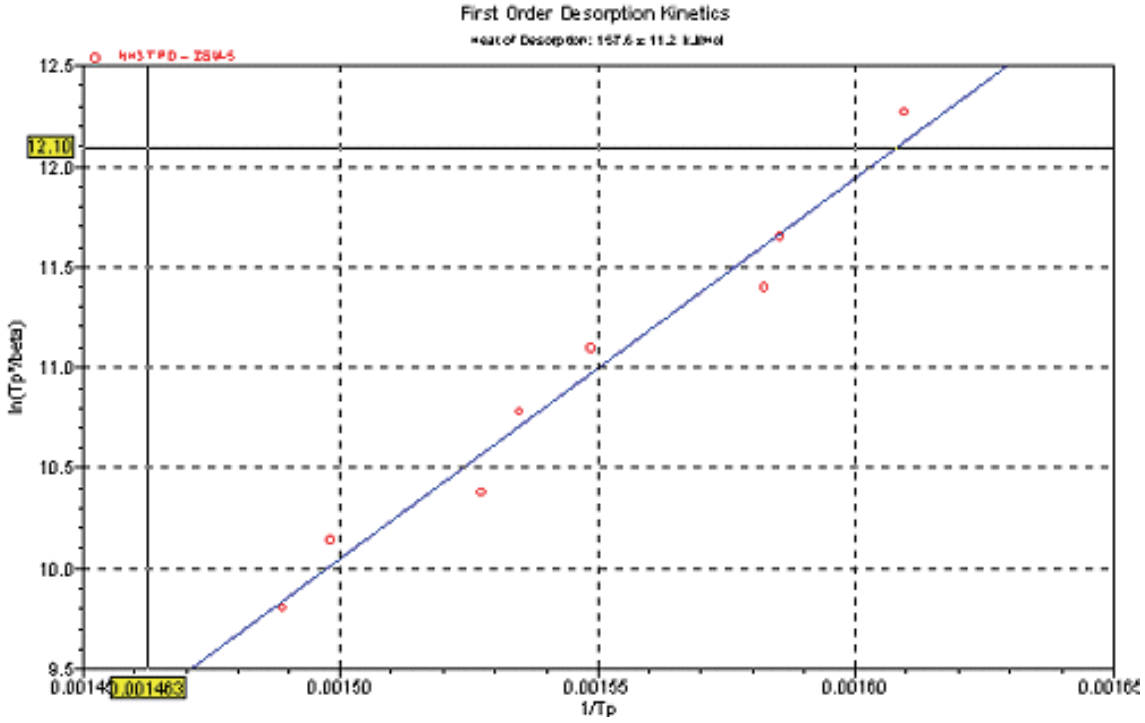

Figure 1b. The Heat of Desorption report is a graphical representation of the determination of heat of desorption. The numerical value of heat of desorption is calculated from the slope of the regression line.