

Searching for the Optimum Adsorption Temperature by the use of the Temperature-Programmed Adsorption (TPA) Technique

By: *Dr. Simone Yunez, Laboratorio de Caracterización de Catalizadores, INTEVEP, Research Centre of Petróleos de Venezuela, Los Teques, Venezuela* email: zamoraju@pdvsa.com Yunezs@pdvsa.com

A temperature-programmed adsorption technique has been applied at INTEVEP, Petróleos de Venezuela, to investigate the optimum temperature for H₂ chemisorption on cobalt-supported catalysts. It has been seen that selecting the appropriate adsorption temperature makes a large difference on the measured value of the dispersion. Moreover, this technique can be extended to any adsorption system regardless of its adsorbate and adsorbent components.

Introduction

Selection of the optimum chemisorption temperature for a specific adsorbate in catalysis has been and still is a matter of investigation. Usually this temperature is selected to be near ambient (35 °C) for convenience. Thus, the selected temperature could be far from the appropriate temperature at which the chemisorption process is activated. Using a wrong

adsorption temperature could yield lower values for the dispersion of the active metals on catalysts. Hence, the use of the temperature-programmed adsorption (TPA) technique would lead to the correct activation temperature and, therefore, to the correct values for the different parameters of the catalyst. A series of cobalt-loading-supported-silica catalysts has been studied. The unique purpose was to determine the optimum H₂ chemisorption temperature, and therefore to relate the volume of the chemisorbed hydrogen to the dispersion and the active metal on the catalyst. A temperature-programmed desorption and reduction (TPD/TPR) Micromeritics instrument, the AutoChem 2920, has the capability of reducing the initial temperature below ambient. The instrument was coupled to an Omnisorb Mass Spectrometer to follow the H₂ signal to ensure the correctness of the thermal conductivity detector (TCD) response. A mass of

about 0.2 g of the original sample has been taken for each experiment. First, the sample was reduced following a TPR profile with a mixture of 5% H₂ in argon. The ramping temperature was 10 °C/min up to the calcination temperature (450 °C). The reduction process was then kept isothermal until the TCD response returned to baseline, to avoid any possible sintering of the active phase. Just after reduction was completed, the sample temperature was reduced to -10 °C under a continuous flow of the reducing mixture (5% H₂ in argon), which was also used for the subsequent experiments. Once the TCD signal returned to baseline indicating the equilibration of the experiment and possible saturation with H₂ of the sample, the sample temperature was then programmed to increase 10 °C/min up to 200 °C. At this point, any possible activity (adsorption and/or desorption of H₂) by the sample was recorded by

both the TCD and the Mass Spectrometer.

Results

The TPA profiles showed a fairly symmetric peak at about 100 °C. On the other hand, the Mass Spectrometer, which was connected at the exit of the TCD, demonstrated that this peak corresponds to the consumption of H₂ by the catalyst. This same experiment was repeated several times to ensure reproducibility of the peak position. All experiments gave almost identical TPA profiles.

Now having established the optimum temperature for H₂ chemisorption for these particular catalysts by TPA, complementary experiments were necessary to ensure that 100 °C was really the optimum temperature at which H₂ uptake is maximum. Four samples from the same original batch were taken for these new experiments using the Micromeritics ASAP 2010 high vacuum system to obtain the adsorption isotherms. The sample was first reduced at 450 °C for 4 hours, and then submitted to high vacuum for 4 hours to ensure the complete elimination of any excess H₂ remaining after reduction.

Each reduced sample was tested for H₂ chemisorption at different analysis temperatures; 35, 70, 100, and 140 °C. The adsorption isotherm was obtained by increasing the H₂ pressure from 10 mmHg to atmospheric pressure. The uptake of H₂ at the monolayer was determined from the extrapolation of the adsorption isotherm to the y-axis (absolute pressure in mmHg). Results of these experiments are plotted in Figure 1. The dispersion and the active metal surface area were obtained according to the classical methods of calculation.

Conclusion

It can be concluded from these results that the TPA technique is a very powerful tool for use in determining the appropriate analysis temperature for chemisorption. The technique could be used and applied for any process of this kind regardless of the adsorbate and adsorbent in use. Combination of the volumetric, the flowing and the Mass Spec-

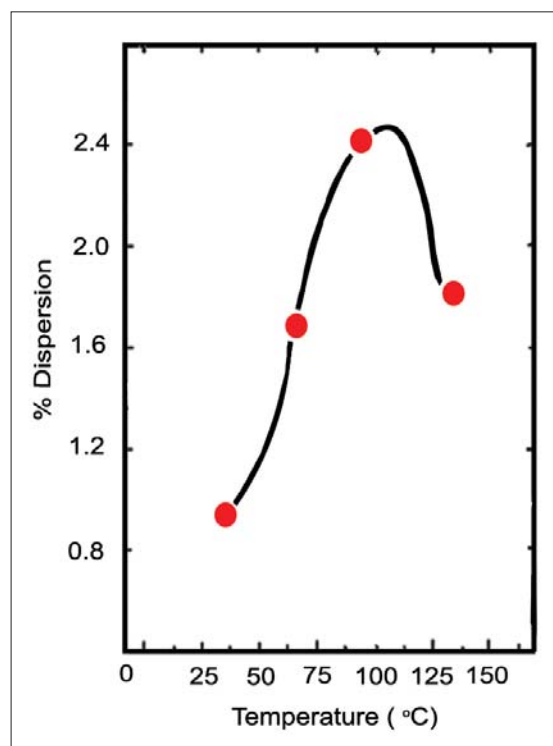


Figure 1 shows the variation of the % dispersion as function of the analysis temperature.

trometer systems should yield definitive results in many other applications in catalytical processes. A catalyst characterization laboratory should combine as many different techniques as possible to ensure complete knowledge of the catalyst properties. This will permit the activity and selectivity of the catalyst to be known long before being loaded into reactors and high expenses incurred.