Temperature-Programmed Reduction

Theory

Temperature-programmed reduction (TPR) is a widely used tool for the characterization of metal oxides, mixed metal oxides, and metal oxides dispersed on a support. The TPR method yields quantitative information of the reducibility of the oxide's surface, as well as the heterogeneity of the reducible surface. TPR is a method in which a reducing gas mixture (typically 3% to 17% hydrogen diluted in argon or nitrogen) flows over the sample. A thermal conductivity detector (TCD) is used to measure changes in the thermal conductivity of the gas stream. The TCD signal is then converted to concentration of active gas using a level calibration. Integrating the area under the concentration vs. time (or temperature) yields total gas consumed. Figure 1 shows a TPR profile for the reaction where M_xO_y is a metal oxide.

$M_xO_y + yH_2 \rightarrow xM + yH_2O$

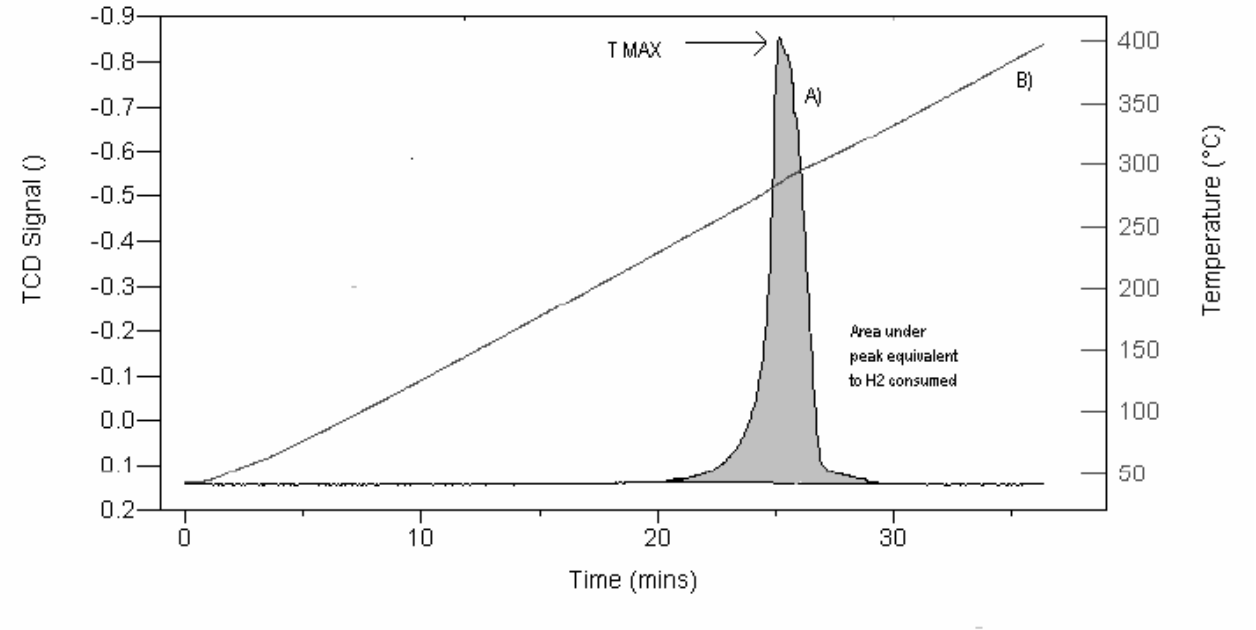

Figure 1. *Temperature-programmed reduction profile for a metal oxide. Trace A displays the TCD signal output as a function of time. Trace B displays the temperature as a function of time during a 10 °C heating rate from ambient to 400 °C.*

This figure illustrates a TPR spectrum where the peak maximum indicates the temperature that corresponds to the maximum rate of reduction. The TPR method provides a qualitative, and sometimes quantitative, picture of the reproducibility of the catalyst surface, as well as its high sensitivity to chemical changes resulting from promoters or metal/support interactions. Therefore, the TPR method is also suitable for quality control of different catalyst charges since deviations in manufacturing methods often result in different reduction profiles.

Experiment

1) Preparation of Ag_2O

$$AgNO_3 + NaOH \rightarrow AgOH + NaNO_3$$

$2\ AgOH \rightarrow Ag_2O + H_2O$

Material: NaOH, $AgNO_3$

Procedure: Calculate the amount of NaOH (excess of 10%) and $AgNO_3$ for preparation of 2 g Ag_2O and weigh them. Prepare 10 % solutions of both. The first reaction is realized by mixing of both solutions with continuous stirring. Filter the precipitate using funnel, wash properly with water, ethanol and dry it in drying box (2 hours). Silver oxide formed in drying box.

2) TPR

Weight ca. 0,06 g of Ag_2O and insert to the reactor. Next, you are mixing liquid nitrogen and isopropyl alcohol preparative of liquid coolant. Assistant set up the instrument Autochem and measure TPR curve.

3) Evaluation

The specific reaction is $AgO + H_2 \rightarrow Ag + H_2O$.

Calculate the theoretical hydrogen consumption for this reaction. You compare this value with measurement value. Determine the temperature of reaction.