Understanding Temperature-Programmed Reduction (TPR) for Catalysis: Parameters and Profiles

1. Background

Temperature-programmed reduction (TPR) is a powerful chemisorption technique for obtaining direct information on the reducibility of catalysts and catalyst precursors. It is widely used to characterize a variety of catalyst materials. In a typical TPR experiment, the sample is exposed to a flowing mixture of a reducing agent (such as hydrogen diluted in an inert gas) which chemically binds to the sample surface in a reaction called chemisorption. At the same time, the sample temperature is increased linearly, and the consumption rate of the reducing agent is continuously monitored and correlated to the reduction behavior of the sample.

Figure 1 presents a representative TPR profile for a 10% NiO/SiO_2 catalyst. The resulting profile provides insights into both the ease of reducibility (indicated by the temperature at the reduction peak maximum) and the extent of reducibility (reflected by the signal area).

A comprehensive description of TPR methodology can be found in *Temperature-Programmed Reduction for Solid Materials Characterization* by A. Jones and B.D. McNicol (Marcel Dekker, Inc., 1986).
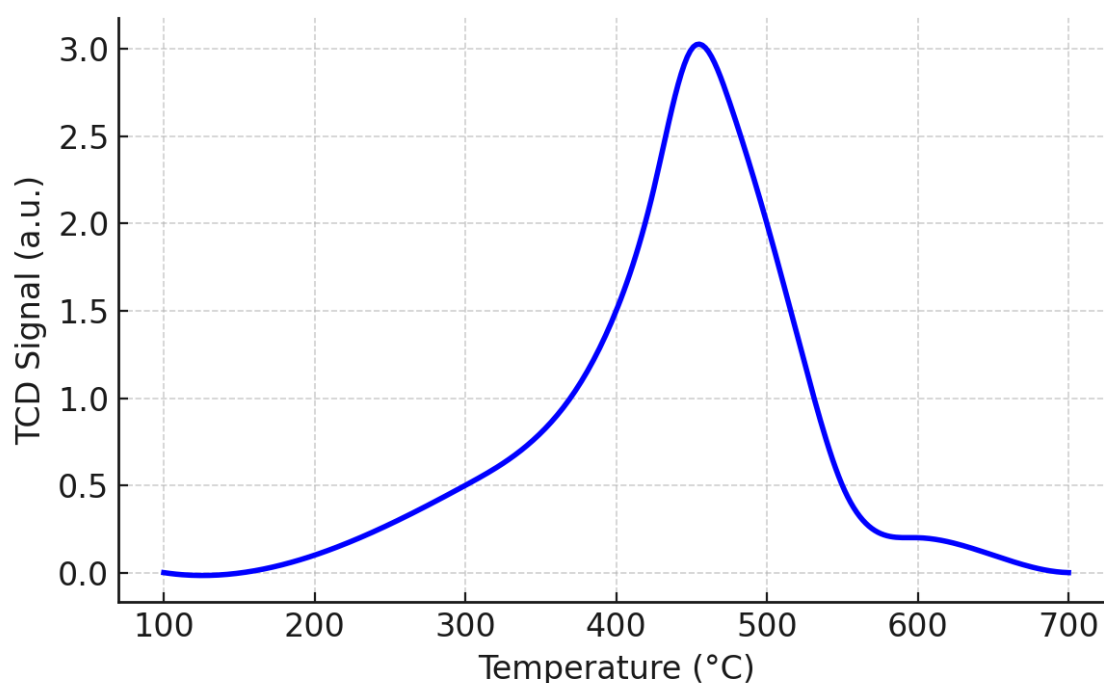

Figure 1. Temperature-programmed reduction (TPR) profile of a 10% NiO/SiO_2 catalyst (10% H_2/Ar, 30 mL/min, heating rate 20 ^oC/min).

2. Importance of Experimental Conditions

Comparing TPR results across different laboratories or literature reports can be challenging. No universally accepted experimental parameters exist for TPR experiments. Variables such as heating rate, reducing gas composition, flow rate, and particle size can all significantly influence the reduction profile. This AMI Note explores the impact of key experimental parameters on TPR results. Monti and Baiker[1] developed an equation that relates the peak temperature (T_m) to the linear heating rate and hydrogen concentration for a first-order reduction process, as follows:

$$\ln(T_m^2)\frac{[H_2]}{rT} = \frac{E_a}{T_m} + \ln\left(\frac{E_a}{RA}\right)$$
Eqn. 1

where:

T_m is the temperature at maximum signal;

$[H_2]$ is the average hydrogen concentration;

rT is the linear heating rate;

E_a is the activation energy of reduction;

R is the gas constant; and

A is a pre-exponential factor.

This equation predicts a decrease in T_m with increasing hydrogen concentration and with decreasing heating rate. It also predicts that the observed temperature maximum is independent of flow rate—a prediction that is **not** supported by experimental observations.

The primary value of this equation lies in its ability to compare data obtained under different conditions. For example, Gentry and coworkers, in a study of CuO, determined E_a to be approximately 67 kJ/mol.[2] Using a flow rate of 20 mL/min, a heating rate of 6.5 °C/min, and a H_2 partial pressure of 0.1, they observed T_m = 280 °C. Applying their results to Equation 1, it becomes possible to predict T_m for other experimental conditions. Figure 2a illustrates how the predicted T_m for CuO would vary with different hydrogen concentrations and linear heating rates according to Equation 1.

The effects of flow rate are more complex and less easily predicted. Intuitively, one would expect T_m to decrease with increasing flow rate, and this trend is confirmed in the literature. Monti and Baiker observed a decrease in T_m of 15°C for supported NiO when the total flow rate was increased from 30 mL/min to 60 mL/min.[1] Similarly, in TPR studies of CuO using 5% H_2 and a heating rate of 20 °C/min, increasing the flow rate from 30 mL/min to 80 mL/min resulted in a T_m decrease of 15°C. As a general guideline, a doubling of the flow rate typically results in a T_m decrease of approximately 10–20°C.

Because TPR is a bulk process, not all particles are exposed to the reducing gas simultaneously,

making T_m dependent on particle size. However, predicting this dependence is complicated by the specific reduction mechanism involved. Lemaitre examined this dependence across different reduction mechanisms,[3] highlighting two that are especially relevant for catalysis:

- **Phase-boundary-controlled reduction**, typical of bulk oxides, and

- **Nucleation-controlled reduction**, typical of supported metals

Interestingly, the predicted relationship between T_m and particle size varies with the reduction mechanism. For bulk oxides, T_m increases with particle size, whereas for supported metals, T_m decreases as particle size increases.

These various factors—and their combined effects on the TPR profile—are summarized in Figure 2b. All should be carefully considered when comparing data from different laboratories or experimental setups.
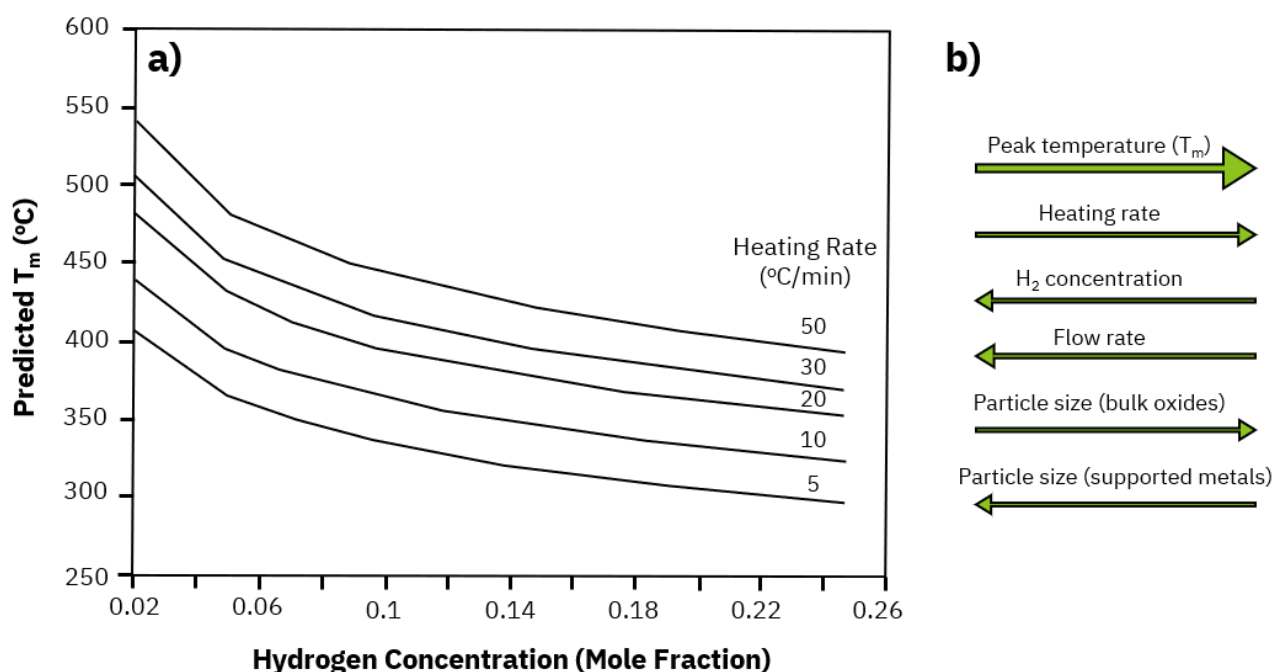

Figure 2. a) Effect of hydrogen concentration and heating rate on predicted T_m for CuO, and b) the relationship between experimental parameters and the observed T_m in TPR experiments

3. References

(1) Monti, D. A. M., and Baiker, A. Temperature-programmed reduction. Parametric sensitivity and estimation of kinetic parameters. *J. Catal*, **1983**, *83*, 323-335.

(2) Gentry, S. J.; Hurst, N. W.; Jones, A. Temperature programmed reduction of copper ions in zeolites. *J. Chem. Soc., Faraday Trans. I*, **1979**, *75*, 1688.

(3) J.L. Lemaitre, in *Characterization of Heterogeneous Catalysts*, F. Delannay (Ed.), Marcel Dekker, Inc., 1984.

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