



EFFECT OF SOME EXPERIMENTAL PARAMETERS ON TPR PROFILES

Temperature-programmed reduction (TPR) techniques can yield direct information on the reducibility of catalysts and catalyst precursors and is an excellent technique for characterizing a variety of catalysts. The technique consists of exposing the sample to a flowing mixture of a reducing agent, such as hydrogen, in an inert gas while linearly ramping the temperature. The rate of consumption of the reducing agent is monitored and related to the rate of reduction of the sample. Figure 1 shows the TPR profile obtained for a 10% NiO/SiO₂ catalyst using a 10% H₂/Ar mixture at a flow rate of 30 ml/min and a linear heating rate of 20 K/min. Such a signal gives information concerning the ease of reducibility (temperature at maximum) as well as the extent of reducibility (signal area) of the material being studied. An excellent comprehensive description of this technique is found in the book "Temperature-Programmed Reduction for Solid Materials Characterization" by A. Jones and B.D. McNicol (Marcel-Dekker, Inc., 1986).

Unfortunately, it is sometimes difficult to compare results obtained in different laboratories or reported in the literature. There exist no optimum experimental parameters for conducting TPR experiments and parameters such as the rate of heating, the composition of the reducing mixture, gas flow rate, and particle size can all greatly affect the rate of reduction. This Altamira Note examines the effect of some experimental parameters in the resulting TPR signal.

Monti and Baiker¹ derived an equation relating the temperature at maximum, T_m, to linear heating rate and hydrogen concentration for a first order process, i.e.:

$$\ln(T_m^2) \frac{[H_2]}{rT} = \frac{E_a}{RT_m} + \ln \frac{E_a}{RA} \quad \text{Eq. 1}$$

where:

- T_m is the temperature at maximum signal;
- [H₂] 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 further predicts that the observed temperature maximum is independent of flow rate, a prediction which is not borne by experiments.

The usefulness of this equation is in comparing data obtained under various conditions. For example, Gentry and coworkers² in a study of CuO determined E_a to be approximately equal to 67 KJ/mole. Using a flow rate of 20 ml/min, a heating rate of 6.5 K/min, and H_2 partial pressure of 0.1, they observed $T_m = 280^\circ C$. Using their results and equation (1) it is thus possible to predict T_m for other experimental conditions. Figure 2 shows how the predicted T_m would vary for CuO for various hydrogen concentration and linear heating rates according to equation (1).

The effects of flow rate are not as easy to predict. Intuitively, one would expect a lowering in T_m with increasing flow rate. This is indeed in agreement with literature reports. Monti and Baiker found a lowering in T_m for supported NiO of $15^\circ C$ as the total flow rate was changed from 30 ml/min to 60 ml/min¹. In the TPR of CuO, using 5% H_2 and a heating rate of 20 K/min, a change in flow rate from 30 ml/min to 80 ml/min resulted in a lowering of T_m by $15^\circ C$. A good rule of thumb is to expect a lowering in T_m of about 10-20'C with a doubling of flow rates.

Since TPR is a bulk process, not all the particle is exposed to the reducing gas at the same time and thus a dependence of T_m on the size of the particle is expected. The prediction of this dependence is complicated by the mechanism by which reduction occurs. Lemaitre³ has examined this dependence for various types of reduction mechanisms, of which perhaps the most important ones from a catalytic viewpoint are:

phase-boundary-controlled reduction, typical of bulk oxides;
and nucleation-controlled reduction, typical of supported metals.

Interestingly, the predicted behavior of T_m with particle size is different depending on the reduction mechanism. For bulk oxides, an increase in T_m is predicted with increasing particle size. The opposite is predicted for supported metals.

These various factors and their effect on the ultimate TPR profile are summarized in Figure 3. They should all be taken into consideration when attempting to compare data taken in different laboratories or under different conditions.

References

- 1) D.A.M. Monti and A. Baiker, J. Catal. 83, 323 (1983)
- 2) S.J. Gentry, N.S. Hurst, and A. Jons, J. Chem. Soc; Faraday I, 75, 1688 (1979)
- 3) J.L. Lemaitre, in "Characterization of Heterogeneous Catalysts", (F. Delannay, ed.) Marcel-Dekker, Inc.

10% Ni/SiO₂ TP REDUCTION

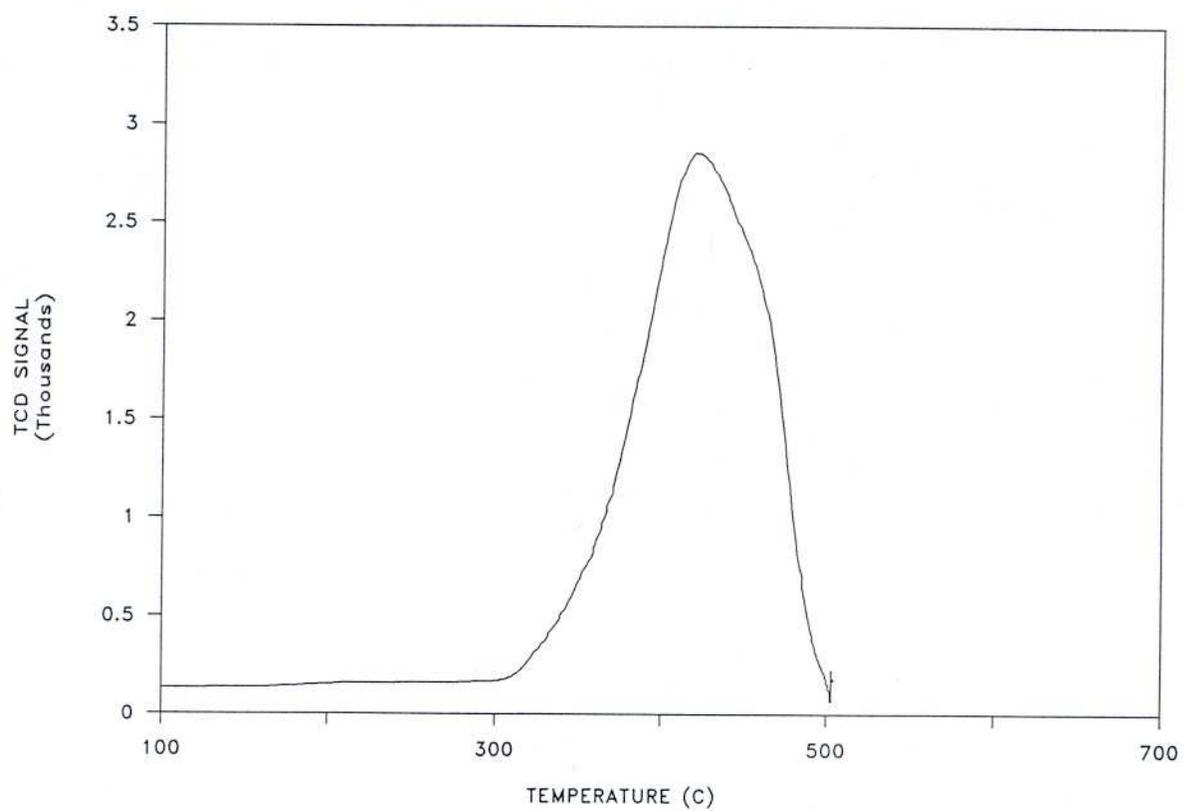


Figure 1. TPR of NiO/SiO₂.

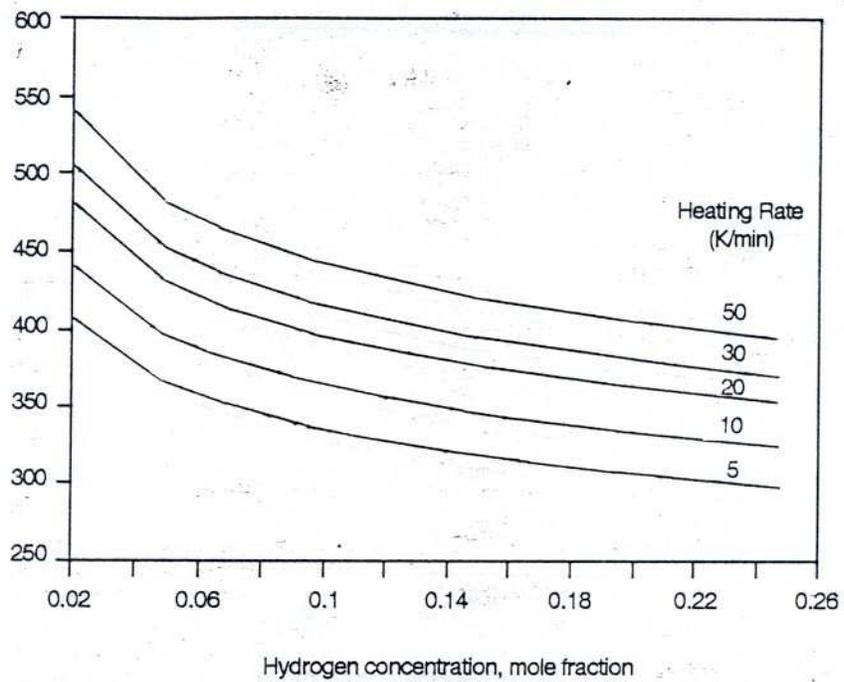


Figure 2. Effect of various TPR parameters on predicted T_m for CuO.

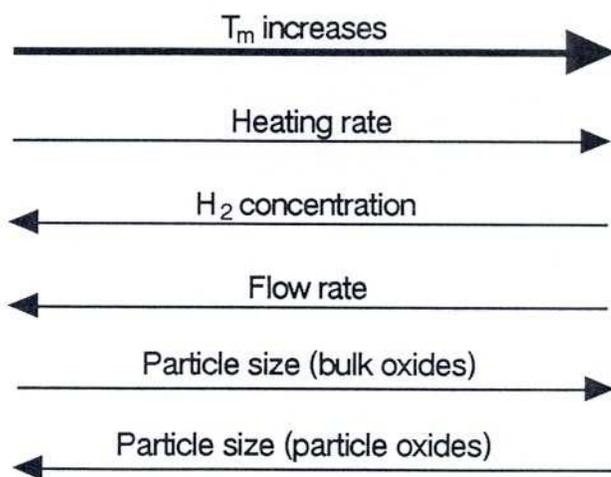


Figure 3. Relation between various parameters and observed T_m in TPR.