B-T-013

H_2 TPR measurement for CuO by BELCAT

Introduction.

TPR stands for Temperature Programmed Reduction (Reaction) and is used as a method to evaluate the reduction of catalysts by hydrogen. There are many applications such as supported copper catalysts1), heteropoly acids2), nickel-based catalysts3), oxides such as Bi-Mo and Fe-Sb4), supported V2O55), and Re catalysts6). TPR is more sensitive to experimental conditions than TPD, especially the concentration of active gas (H2), gas flow rate, and catalyst volume, so it is necessary to pay attention to these factors. In the experiment, the change in the concentration of hydrogen gas components in the carrier gas or the amount of reaction products is recorded as a function of time or temperature during the temperature rise. In this case, the apparatus for TPD can be used almost as is, but if TCD is used as the detector, an H2O trap must be attached in front of the detector. The following equation has been proposed to calculate the activation energy Er from the TPR curve.

$$\ln\left(\frac{T_P^2}{\beta}\right) + p\ln[G]_m + (q-1)\ln[S]_m = \frac{E_r}{RT_P} + const. \qquad (1)$$

where [G]m and [S]m are the hydrogen gas concentration and catalyst concentration at the peak temperature, respectively, and p and q are the reaction order for each. In general, it is impossible to determine the exact values of p and q, so it is common to set p=q=17).Iwamoto et al. measured the TPR of copper ion-exchanged Y-type zeolite (CuNaY) in the range of 273 to 1123 K (Fig. 1).8)

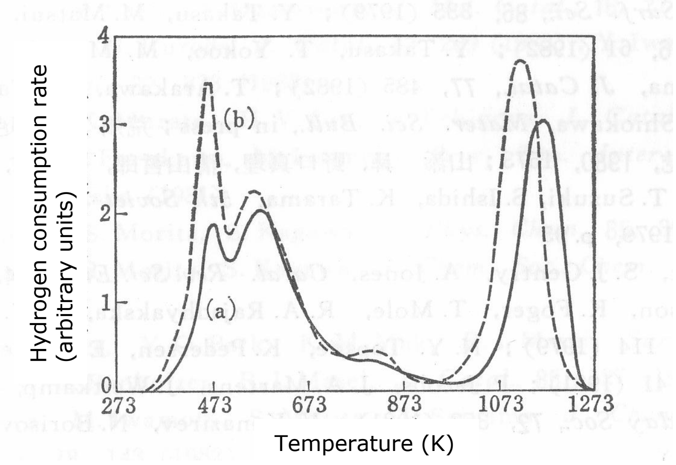

Fig. 1 TPR curve of CuNaY

The results show that four reduction peaks appear at 473(I), 593(II), 803(III), and 1123(IV). The hydrogen consumption is about 0.5 mol(H2)/mol(Cu) in the range of 273 to 773 K and 773 to 1273 K, respectively; all ESR spectra of Cu2+ disappear at 773 K reduction; the color of the sample changes from blue-green (273 K) to white (≈773 K) to reddish brown (>800 K). The TPD curve of CuNaY reduced at 473K shows a TPD peak 9) that can be attributed to Cu-O-Cu. They attributed the four reduction peaks to the following reduction processes.

$2Cu^{2+}+H_2 \rightarrow 2Cu^{+}+2H^{+}$	**(Peak I)**
$Cu^{2+}\text{-}O^{2-}\text{-}Cu^{2+}+H_2 \rightarrow 2Cu^{+}+H_2O$	**(Peak II)**
$2Cu^{+}+H_2 \rightarrow 2Cu^{0}+2H^{+}$	**(Peak III, IV)**

This method has been extended to Cu2+ exchangers of mordenite and ZSM-5[10] and has become a powerful method for elucidating the properties of metal ions in zeolite frameworks. In some cases, the total amount of reduction is determined by measuring the amount of chemisorption using oxygen pulses after TPR measurement and cooling to around room temperature. This method is considered to have poor reproducibility of TPR and problems with the linearity of the detector.

Experiments and results

In the TPR experiment, the change in hydrogen concentration can be detected by TCD, but in the case of He carrier gas, it is known that the difference in thermal conductivity with H2 is small and detection is difficult. However, in the case of He carrier gas, it is known that the difference in thermal conductivity between He and H2 makes detection difficult. In other words, in most cases, Ar diluted H2 carrier gas is used for TCD detection, and it is necessary to trap the water generated by the reduction reaction in front of the TCD detector.

As an example of measurement, we will introduce the case of H2-TPR measurement of CuO using BELCAT.

Measurement device : BELCAT
Detector : TCD (semi-diffusion type 4 elements)
Sample used : CuO
(Wako Pure Chemical Industries Lot No. APJ4311)
Gas used : 5% H2/Ar
Temperature rise rate : 10 °C/min.

pretreatment program

Gas used	min	Target temperature
1:H2/Ar	60	30

Measurement program

TCD stability latency	20 min
Target temperature	1000 °C
Temperature rise rate	10 °C/min
Target temperature holding time	30 min

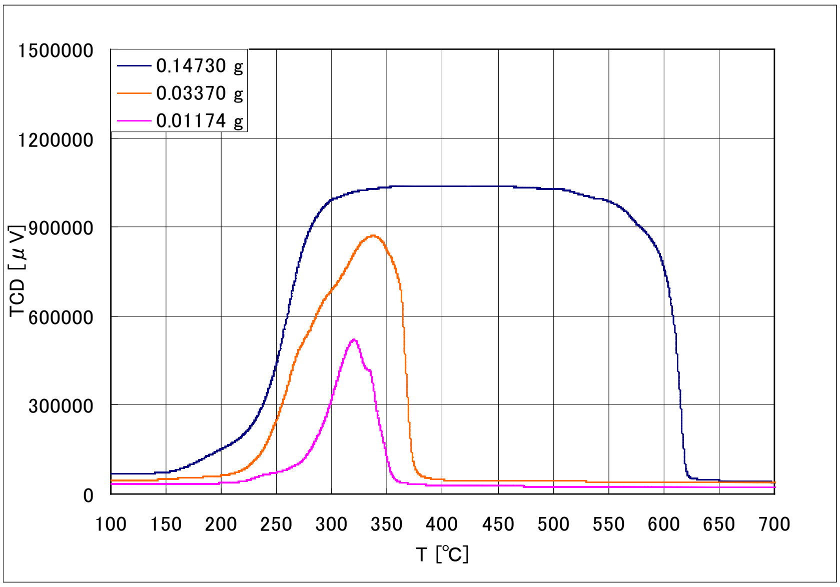

Figure 2. CuO TPR spectrum

As can be seen from Figure 2, the shape of the peak changes remarkably just by changing the sample weight. The peak shape at a sample weight of 0.14g is completely consumed by the introduced hydrogen and the hydrogen concentration change is saturated. If such a spectrum is obtained, it is better to reduce the sample weight or increase the hydrogen concentration in the carrier gas.

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