B-AD-033

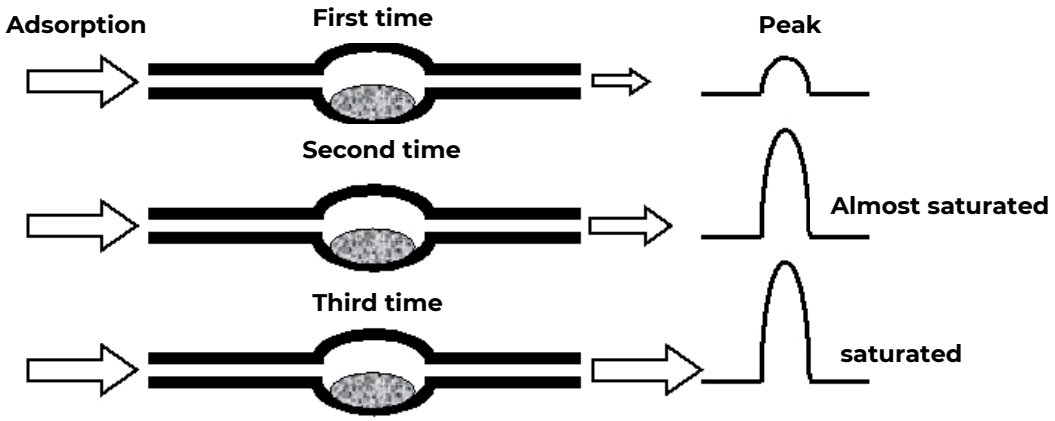
Metal dispersion rate measurement by pulse method

Introduction

Metal-supported catalysts are essential material for variety of catalitic reactions, and much research is being done to improve their activity and efficiency.
In metal-supported catalysts, increasing the surface area of the metal increases the active site of the reaction and increases the catalytic efficiency. In addition, even if the metal loading is the same, more metal surface area can be obtained by increasing the metal dispersion. Especially in the case of expensive precious metal supported catalysts, research and development of high dispersibility and suppression of degradation (decrease in dispersibility) is underway as a method to maintain high activity while reducing the amount of support in order to reduce costs.
Pulse adsorption method is generraly used as quick characterization method because of its high accuracy and short measurement time. This paper describes the metal dispersion rate measurement by pulse method using the catalyst analyzer [BELCAT].

Experiment

2.1 Principle of measurement
Pulse the adsorbed gas into the sample in the carrier gas stream until it reaches saturation, and calculate the gas consumption from the difference in area between the pulse peak at saturation and the pulse peak.



The calculation method is shown below.

Unit adsorption capacity [adsorption capacity per gram of sample] /$cm^3 \cdot g^1$

$$Vm = V_{Chem} / m$$

V_{chem} : adsorption volume/cm^3
m : Sample weight /g

Metal dispersion [percentage of metal surface exposed] /%.

$$Dm = \frac{V_{Chem} \times SF / 22414 \times MW}{c} \times 100$$

V_{chem} :adsorption volume/cm^3
MW :Metal atomic weight /g・mol^{-1}
m : sample weight / g
SF : Stoichiometric factor (stoichiometric ratio)

Metal weight [weight of metal supported on sample] /g

$$c = m \times p / 100$$

p : Supported metal content/%.

Metal surface area [metal surface area per gram of sample] /m^2 • g-1

$$Am(Sample) = \frac{V_{Chem} \times SF / 22414 \times 6.02 \times 10^{23} \times \sigma_m \times 10^{-18}}{m}$$

σ_m :Metal cross-sectional area of one atom/nm^2

Metal surface area [metal surface area per gram of supported metal] /m^2 • g-1

$$Am(Metal) = \frac{V_{Chem} \times SF / 22414 \times 6.02 \times 10^{23} \times \sigma_m \times 10^{-18}}{c}$$

Metal particle size [diameter of metal particles as spheres] /nm

Area per gram of metal: $\frac{4\pi r^2 \times \alpha}{c} = Am(Metal)$ (1)

r : radius of metal particle/m

α: Number of metal particles

Volume per gram of metal : $\frac{4/3\pi r^3 \times \alpha}{c} = 1/(\rho \times 10^6)$ (2)

ρ :Metal density/g • cm^{-3}

From (2)/(1) : $r/3 = (Am(Metal) \times \rho \times 10^6)$

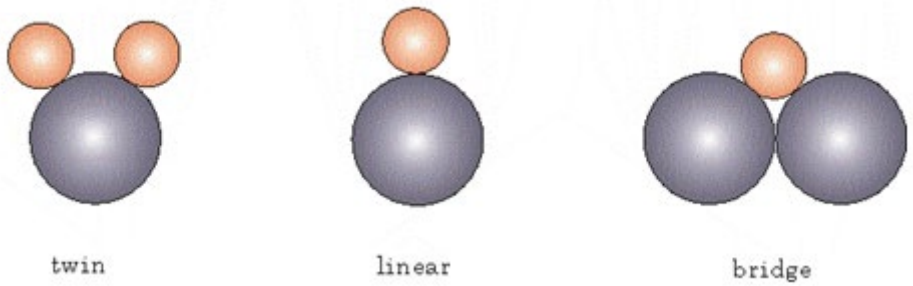
$$r = 3/(Am(Metal) \times \rho \times 10^6) \quad (3)$$

Metal particle size $d = 2r \times 10^9$

Substitute (3) : $d = 6/(Am(Metal) \times \rho \times 10^6) \times 10^9$

$$d = 6000/(Am(Metal) \times \rho)$$

Stoichiometric factor [SF] is necessary to calculate above calculation. This is a number that indicates how many metal atoms are adsorbed by one adsorbed gas molecule. It is depends on the form of chemisorption of the adsorbed gas.
There are three types of CO chemisorption: Linear type [SF: 1], in which one CO molecule is adsorbed on one metal atom; Bridge type [SF: 2], in which one CO molecule is adsorbed on two metal atoms; and Twin type [SF: 0.5], in which two CO molecules are adsorbed on one metal atom. The adsorption structure of such molecules on supported metal particles can be determined by infrared spectroscopy (IR). The morphology of adsorption is influenced by the properties of the metal: CO adsorption on Cu, Ag, and Au is weak and is easily desorbed by evacuation at room temperature; linear type is dominant for Fe, Pt, and Ir; bridge type is dominant for Pd, Ni, and Co [especially Pd]; twin type can be seen for Rh.
H2 dissociates to H+ and is chemisorbed by linear adsorption, where one H^+ is adsorbed per metal atom, but its adsorption force is generally weaker than that of CO [SF:2]. These may vary depending on the support structure of the metal and the coverage of the adsorbed gas.



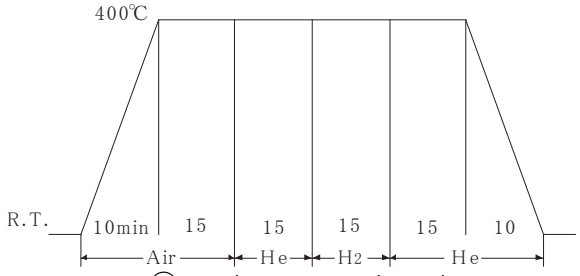
2. measurement method

The metal dispersion rate measurement is performed by introducing a pulse of adsorbed gas into the pretreated sample in a carrier gas stream. The following two points should be noted in the measurement.

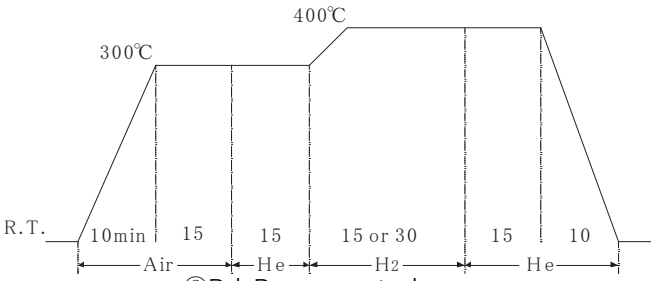
1. When using a TCD detector, He is used as the carrier gas for CO pulse measurements, and Ar is used for H2 pulse measurements. Because thermal conductivity should be different enough between carrier and adsorption gas to detect by TCD.
2. Set the pulse introduction volume or sample volume so that saturation will be reached in 2 or 3 pulses. If the amount is not appropriate, the measurement accuracy will be reduced and takes long time.

Pretreatment

The following two pretreatment patterns are recommended in the "Method for Measuring Metal Surface Area by the CO Pulse Method" established by the Reference Catalyst Committee of the Catalysis Society of Japan. The following two pretreatment patterns are recommended.



①Pt, Rh supported catalysts



②Pd, Ru supported catalysts

Sample amount : 50 to 200 mg
Measurement temperature : R.T.
Gas flow rate : 20 to 40 cm3/min
Pulse volume : 20 to 200 µl (0°C, 1 atm): Volume that reaches saturation in 2 to 3 times
Pulse interval : 2 to 3 min
For the sample weight, use the weight after the measurement is completed.

The purpose of air treatment is to remove organic contamination. The air treatment temperature of 300°C for Pd and Ru is to avoid sintering and redispersion. The reduction time for Ru is

recommended to be 30 min. In addition, the presence of oxygen in the carrier gas (especially for Rh, which has strong binding power with oxygen) may cause a decrease in the adsorption amount.

carrier effect

When measuring a sample with a metal supported catalyst, the metal dispersion rate may not be accurately measured due to [carrier effect].

Carrier effect (1) Spillover

This is a phenomenon in which the metal dispersion rate by the H2 pulse method exceeds 100% for samples such as Pt/C and Pt/Al_2O_3. It is thought that the H^+adsorbed on the metal moves onto the support metal and further hydrogen is adsorbed on the surface of support metal.

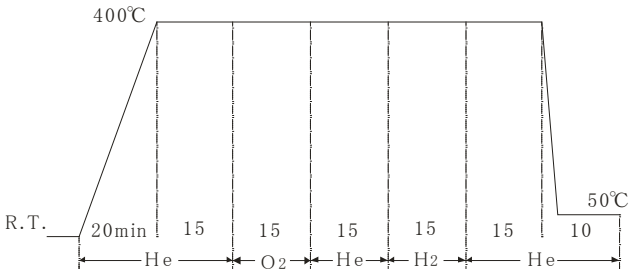
Carrier effect (2) SMSI [Strong Metal Support Interaction].

This is a phenomenon in which the adsorption of H2 and CO on the metal is reduced due to the strong interaction between the supported metal and the support metal. For example, Ni/SiO2 adsorbs H2, while Ni/Al2O3 barely adsorbs.

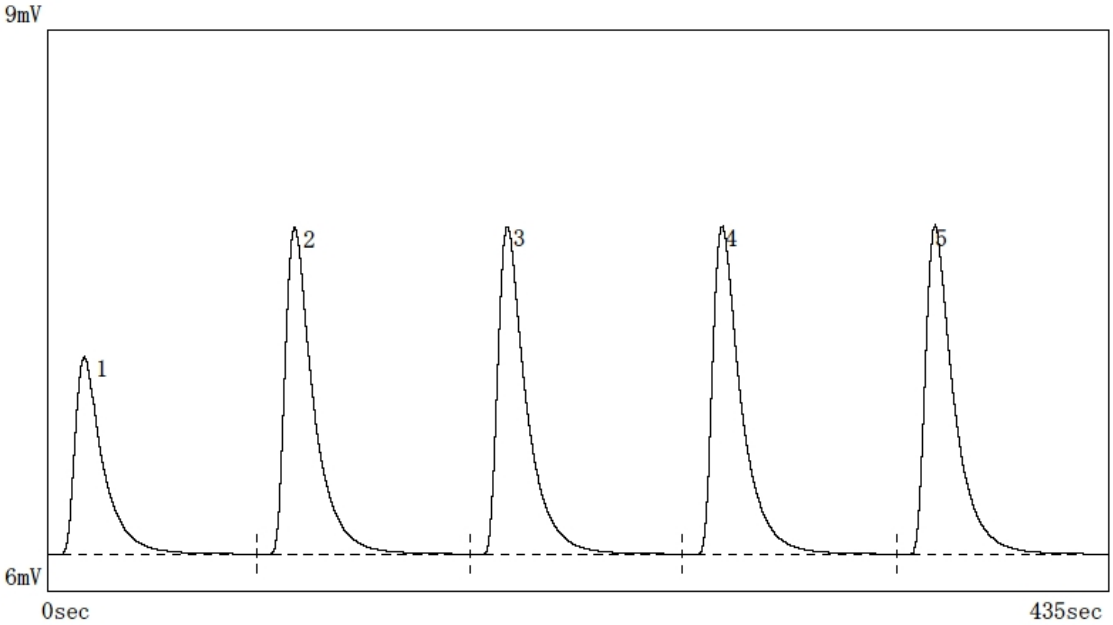
2.3. measurement example

As an example of a typical measurement, we measured the metal dispersion of 2%Pt/Al2O3 using CO pulses.

pretreatment



Instrument : BELCAT
Sample: 50 mg (Reference material : 2%Pt/Al2O3)
Measurement temperature : 50°C
Gas flow rate : 30 cm3/min
Pulse volume : 100µl (0°C, 1atm)



adsorption amount : 0.604 cm3/g
Metal dispersion rate : 25.4 %
Metal surface area (Sample) : 1.30 m2/g
Metal surface area (Metal) : 62.8 m2/g
Average particle size : 4.45 nm

Results and Discussion

The pulse gas used for the measurement is generally CO or H2, it is important to note that the stoichiometric factor of CO changes depending on its adsorption structure. Pulse measurement with appropriate pulse amount provides stable measurement results. (adsorption saturation should be reached after 1-2 pulses)

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