B-AD-027en Determination of metal dispersion rate for metal supported catalyst by titration pulse chemisorption measurement

Introduction.

Metal-supported catalysts are used industrially for hydrogenation, dehydrogenation, and isomerization reactions, and play an important role in these processes. In these metal-supported catalysts, as the dispersion of the metal increases, the number of active sites for the reaction not only increases, but also the contribution of atoms at the corners and edges of the metal particles increases, and the reaction activity and selectivity change due to the interaction between the metal and the individual particles. For this reason, it is very important to know the degree of metal dispersion in the case of metal catalysts. In the case of precious metal catalysts, the amount of support is linked to the cost of the catalyst material, so how to increase the activity with a small amount is an important issue.

Metal dispersion is evaluated by measuring the amount of hydrogen and CO chemisorption. There are three types of CO chemisorption: Linear type, in which one CO molecule is adsorbed on one metal atom; Bridge type, in which one CO molecule is adsorbed on two metal atoms; and Twin type, in which two CO molecules are adsorbed on one metal atom. (Figure 1), where one CO molecule is adsorbed on two metal atoms, and Twin type, where two CO molecules are adsorbed on one metal atom, with stoichiometry factors of 1, 2, and 0.5, respectively. The adsorption structure of such molecules on supported metal particles can be determined by infrared spectroscopy (IR).[6] CO adsorption is strongly affected by the properties of the metal, and the adsorption interaction of CO on Cu, Ag, and Au is weak and desorbed at room temperature. linear type is dominant for Fe, Pt, Ir, etc., bridge type is dominant for Ni, Co, especially Pd, and twin type is predominant for Rh (Table 1). It is also known that the adsorption structure may change depending on the support structure of the metal and the CO coverage.

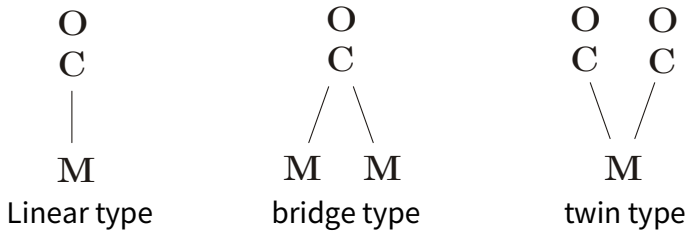

Figure 1. Adsorption type of CO molecule to metal supported catalyst

Table 1 Adsorption type of CO on supported metals and υ(C-O)/cm^{-1}

	linear type	bridge type	twin type
Cu,Ag,Au	2100 to 2160	-Mr.	-Mr.
Fe,Pt,Ir	2000 to 2070	small	-Mr.
Co,Ni,Pd	1980 - 2080	1800-1900	-Mr.
Rh	~2060	~1900	2100,2030
Ru	~2030	~1900	-Mr.

Pretreatment exposes the clean surface of the metal by oxidation and reduction processes at high temperatures. Depending on the metal supported, the metal may be sintered or redispersed, and the pretreatment pattern shown on the right is proposed by the Reference Catalysis Committee[1-3] .

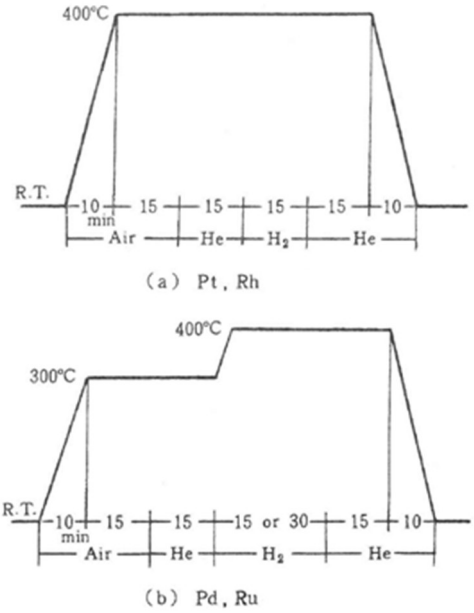

Figure 2 Pretreatment pattern

After the pretreatment, the catalyst is cooled to near room temperature (about 50°C) and then pulsed CO gas is introduced. Normally, chemisorption occurs in the first one or two pulses, and the pulse area becomes smaller than that of the subsequent pulses. The amount of chemisorption is calculated by subtracting the small area of the first two pulses from the area of the first two pulses and continuing until the pulse area does not change.

The metal dispersion, metal surface area, and metal particle size can be calculated using the following calculation parameters.

Calculation parameters

V_{chem} / mol • g^{-1}	: Chemisorption capacity
SF	: Stoichiometric factor
MW	: Atomic weight of supported metal
c/ wt%	: Amount of metal supported
σ_m / nm^2	: Cross-sectional area of supported metal
ρ / g • cm^{-3}	: Density of supported metal

Calculation Formula

Metal dispersion

$$Dm/\% = \frac{\text{Number of chemisorotion site}}{\text{Number of metal atoms held}} \times 100 = \frac{V_{chem} \cdot SF \cdot MW}{c/100} \times 100$$

Metal surface area (per gram of catalyst)

$$A_m\,(m^2/g) = V_{chem} \cdot 6.02 \times 10^{23} \cdot SF \cdot \sigma_m \cdot 10^{-18}$$

Metal surface area (per gram of stretching metal)

$$A_m\,(m^2/g) = \frac{V_{chem} \cdot 6.02 \times 10^{23} \cdot SF \cdot \sigma_m \cdot 10^{-18} \cdot 100}{c}$$

Average particle diameter,

$$S_m\,(nm) = 2r \times 10^9 = \frac{6c}{A_m \times 100 \times \rho \times 10^6} \times 10^9 = \frac{60c}{A_m \times \rho}$$

Due to the following phenomena, the metal particle size (degree of dispersion) evaluated from CO pulses may differ significantly from the geometric size of the metal measured from X-ray diffraction and electron microscopy.

Spill over

In case of metal spported catalyst for Pt/C and Pt/Al2O3, metal dispersion by H2 chemisorption is greater than 1. It is thought that hydrogen is adsorbed on the suport materials.

SMSI

This is an abbreviation for Strong Metal Support Interaction, a phenomenon in which the H2 and CO adsorption capacity of a metal is reduced due to the strong interaction between the supported metal and the single metal.

Experiment

Equipment Device:	BELCATII
Sample :	2% Pt alumina powder from N.E.Chem Cat (Lot No. 137-80110)
Adsorption gas :	CO
concentration :	99.90 %
Supported metal :	Pt
Atomic weight :	195.08
Density :	21.45g • cm $^{-3}$
Metal cross-sectional area :	0.08 nm^2 • atom $^{-1}$
Stoichiometric ratio :	1

pretreatment program

Gas	min	Set temperature/°C
0:He	40	400
0:He	15	400
2:O2	15	400
0:He	15	400
1:H2	15	400
0:He	15	400
0:He	5	50

Measurement program

Adsorption temperature/°C	50
Adsorption gas name	CO
Weighing tube size/cm^3(S.T.P.)	0.3664
TCD stability waiting time/min	10

Time to introduce adsorption gas into the sample tube/sec	30
Waiting time for pressure stabilization in the sample tube/sec	10
Pulse Detection Method	Automatic detection TCD output 0.02% mV/sec
Adsorption equilibrium judgment	Error of final 3-pulse detection within 2

Result

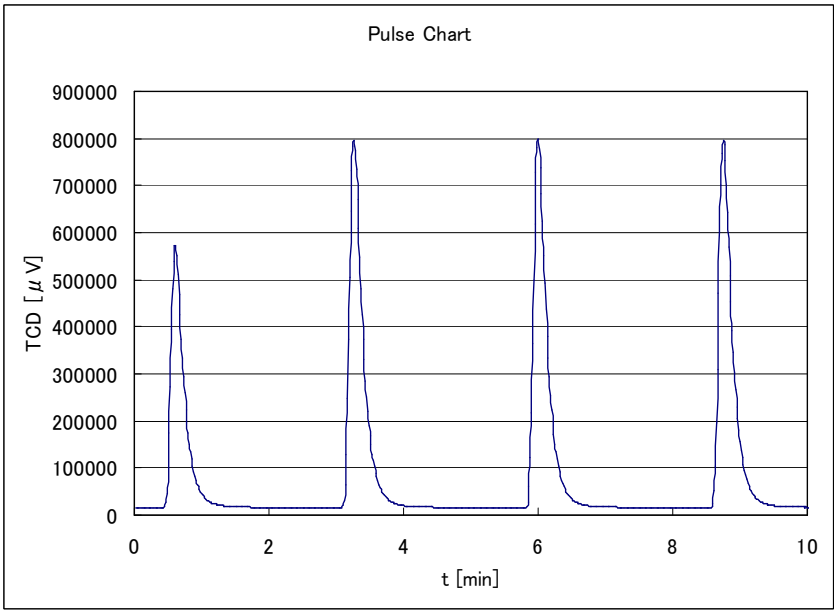

Figure 3. CO pulse titration to 2% Pt alumina powder

Table 2. Metal dispersion, metal surface area and average particle size for 2% Pt alumina powder

Sample weight /g	Pulse chemisorption volume /cm³(S.T.P.)	Chemisorption amount / cm³ · g-1	Metal dispersion	Metal surface area (per g of supported metal)/m² · g-1	Metal surface area (per g of catalyst) / m² · g-1	Average particle size /nm
0.1815	0.367	0.690	30.0	74.2	1.48	3.8
0.1617	0.366	0.678	29.5	72.8	1.46	3.8
0.1560	0.365	0.709	30.8	76.1	1.52	3.7
0.1980	0.367	0.670	29.2	72.0	1.44	3.9
average		0.687±0.015	29.8±0.63	73.8±1.5	1.476±0.0315	3.8±0.08

References

1) Catalysis Society of Japan, Committee on Reference Catalysis, Catalysis, **33**, 249 (1991)

2) M. Niwa, M. Iwamoto, K. Segawa, Bull. Chem. Soc. Jpn. **59**, 3735 (1986).

3) Catalysis Society of Japan, Committee on Reference Catalysis, Catalysis, **31**, 317 (1989)

4) Ken-ichi Akika and Tadashi Hattori, "Handbook of Catalysis Experiments", Catalysis Course (separate volume), 261, Kodansha (1986) (in Japanese).

5） Kasahara, S., Miyabe, S., Shimizu, T., Takase, H., and Yamada, M., Journal of the Japan Petroleum Institute, **38**, 81 (1995).

6） Toshio Okuhara and Makoto Giono, Surface, **18**, 357 (1980)

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APENDIX

Examples of parameters in chemisorption measurements

The following table is a reference example of the parameters required for pulse measurement of metal dispersion using BEL-CAT. These figures are based on past research and are not a guarantee of actual conditions. Please use them as a reference only, and determine the values by checking past literature for details. If the number is blank, there is no information.

Metal	Metal Molecular Weight	Metal density g ^{cm3}	Metal surface area nm2 atom-1	Adsorption gas	S.F.
Pt.	195.080	21.450	0.0800	H_2	2
				CO	1 or 2
Pd (Palladium)	106.420	12.023	0.0787	H_2	2
				CO	1 or 2
Ni (Nickel)	58.693	8.908	0.0649	H_2	2
				CO	1 or 2
Re(renum)	186.207	21.020	0.0649	H_2	2
				CO	1 or 2
Rh (Rhodium)	102.906	12.410	0.0752	H_2	2
				CO	1 or 2
Ru (Ruthenium)	101.07	12.410	0.0614	H_2	2
				CO	1 or 2
Fe (iron)	55.845	7.874	0.0614	H_2	2
				CO	1 or 2
Co (cobalt)	58.933	8.900	0.0662		
Cu (copper)	63.546	8.960	0.0680	N2O	2
Ag (Silver)	107.868	10.500	0.0869		
Au (Gold)	196.967	19.320	0.0870		
MoO_3(MoS2)	127.938			NO.	1
Fe_3O_4	231.533			NO.	1 or 2
CaO	56.079			CO_2	1