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DETERMINATION OF THE DISPERSITY OF METAL ON Ir/Al_2O_3 CATALYST BY THERMOGRAVIMETRY

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ABSTRACT

This paper describes the determination of the metal dispersity of a catalyst by chemical adsorption using a thermogravimetric technique. The metal dispersity of two Ir/Al_2O_3 catalysts for hydrazine decomposition was determined by adsorption measurement using CO as adsorbate and a thermobalance. The results are not exactly identical with those determined by a chromatographic method but they are of the same magnitude and, moreover, the effect of reducing temperature on dispersity is the same in either case. Thus, it is feasible to determine the metal dispersity by thermogravimetry. The effects of the content of active component, Ir, of the reducing temperature and of the environmental atmosphere on the metal dispersity were also investigated.

INTRODUCTION

In general, the catalytic behaviour of the active component of a catalyst is related to its specific surface. When the active component is supported or diluted, it is significant only in the way it affects the usable active surface or particle size of the metal. A large number of experiments have shown that the activity, selectivity and stability of the supported catalyst are closely related to the dispersity of the metal on the support. Therefore, when studying the properties of a catalyst, the determination of the metal dispersity is very important.

The metal dispersity of a supported catalyst may be described in terms of the active surface area and particle size of the metal, which can be determined by chemical adsorption, X-ray diffraction broadening, electronic microscopy, thermomagnetic method, electron probe, etc. [1]. The essential requirement of the widely used chemical adsorption method [2] is that a monolayer of adsorbate is chemisorbed on the metal with no obvious chemical adsorption on the carrier. Thus, the dispersion of metal can be assessed by the amount of adsorption which can be determined by two methods, namely gravimetry and volumetry. A spring balance is usually used in the gravimetric measurement and high vacuum is required; thus, its

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installation is complicated and the operation is time consuming as compared with volumetry and chromatography [3,4]. In this study, the metal dispersity of the catalyst was determined by chemical adsorption using a thermogravimetric technique. The metal dispersity of two Ir/Al_2O_3 catalysts for hydrazine decomposition was determined by measuring the amount of CO adsorbed using a thermobalance; the effects of iridium content, reducing temperature and environmental atmosphere on the metal dispersity were also studied.

BASIC PRINCIPLES

There is a simple relationship between the number of molecules of adsorbate and the number of metal atoms on the surface of the catalyst, provided the adsorbate is chemisorbed in a monolayer. Thus, the number of molecules of adsorbate adsorbed on the metal surface can be calculated from the amount of adsorbate chemisorbed on the metal of the catalyst. If the sectional area of the metal atom and the chemisorbed amount of adsorbate are known, the active surface area or the average grain size of the metal of the catalyst can be calculated.

Falconer et al. [5,6], using chemical adsorption and IR spectroscopy, have found that one CO molecule is adsorbed by two Ir atoms, i.e. the stoichiometric number of CO chemisorbed on iridium is 2. The amount of CO adsorbed in a monolayer at full coverage is 7.1×10^{14} molecules cm^{-2}. Assuming that the active centres are well-distributed on the (100), (110) and (111) faces of low index, its density will be 1.4×10^{15} Ir atoms cm^{-2}. Thus the equations for the calculation of the active surface of the catalyst and the average grain size of metal can be derived from the chemisorbed amount of CO on Ir: the active surface area of metal (S_{Ir}), $S_{Ir} = 2.796 \times 10^5\ \Delta m/mW$ (m^2 per g of Ir) where Δm is the amount of CO adsorbed, m is the amount of sample and W is the iridium content (%); and the average grain size of metal ($\bar{d}$), $\bar{d} = 6/\rho S_{Ir} = 0.268\ 1/S_{Ir} \times 10^4$ (Å) where ρ is the density of metallic iridium (22.4 g cm^{-2}).

EXPERIMENTAL

Materials

1. Catalysts: A, reduced at 400 °C, Ir content 40.2%; B, reduced at 400 °C, Ir content 8, 16.8 and 30.3%; and C, reduced at 200 °C, Ir content 25.5%.
2. Adsorbate: CO, purified by soda-asbestos and activated C.
3. Reducing gas: H_2.

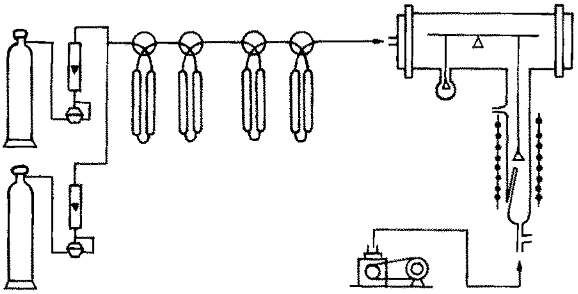

Fig. 1. Schematic arrangement for adsorption measurement.

Adsorption measurement

The experimental apparatus is composed of a purifying system for the adsorbate and a thermogravimetric analysis system. A diagram of the adsorption measurement arrangement is shown in Fig. 1. Adsorption measurement was carried out on a thermobalance of a Shimadzu DT-20B type thermoanalyser with the following experimental conditions: measuring range, 2 mg; heating rate, 10 °C min^{-1}; paper speed, 1.25 mm min^{-1}; and atmosphere, CO.

The catalyst was placed in a quartz basket and weighed by difference. Then the basket was hung on one end of the balance and placed in a quartz reactor. The reactor was evacuated and charged with H_2, and the catalyst was reduced by heating in a temperature programming mode to a given temperature for one hour. The sample was then cooled to 150 °C and the measuring range of the balance was adjusted to 2 mg. The reactor was re-evacuated and recharged with H_2, and the catalyst was reduced completely by heating in a temperature programming mode to a given temperature for 0.5 hour, followed by evacuation and cooling to 150 °C. The reactor was then charged with CO. The adsorption temperature and adsorption amount were recorded with a two-pen recorder.

RESULTS AND DISCUSSION

Metal dispersity of the catalyst measured by thermogravimetry

In order to verify the reliability of the thermogravimetric method, the Ir/Al_2O_3 catalysts A and C of known metal dispersity determined by chromatography were investigated using thermogravimetry. The results are given in Table 1 and a comparison of these two methods is shown in Table 2.

The reproducibility of the metal dispersity of the catalyst as determined by the thermogravimetric method is very good and the relative error is

TABLE 1

Amount of CO adsorbed and metal dispersity of Ir/Al_2O_3 (average value of duplicate test)

Catalyst [a]	Sample weight (mg)	CO adsorbed (mg)	Ir content (%)	S_{Ir} (m^2/g Ir)	Δ (%)	$\bar{d}$ (Å)	Δ (%)
C	74.61	0.83	25.5	129.6	2.7	20.6	2.8
A	76.22	0.70	40.2	64.4	5.1	41.6	5.1

[a] Reduced at 400 °C.

TABLE 2

Comparison of the dispersities determined by thermogravimetric and chromatographic methods

Catalyst	Reducing temperature (°C)	Ir content (%)	Thermogravimetric		Chromatographic	
			S_{Ir} (m^2/g.Ir)	$\bar{d}$ (Å)	S_{Ir} (m^2/g.Ir)	$\bar{d}$ (Å)
C	200	25.5	126	21.3	147.9	18.1
A	400	40.2	64.4	41.6	25.6	104.6

within 5% (Table 1). The results are not exactly the same as those determined by chromatography, but they are of the same magnitude. Moreover, the same effect of reducing temperature on dispersity is observed in either case. This demonstrates that thermogravimetry is a reliable method for comparative analyses.

Effect of the active component content in the catalyst on dispersity

To examine the effect of Ir content on dispersity, the dispersity of catalysts B with different Ir contents reduced at 400 °C were determined by thermogravimetry (Table 3). The dependence of Ir content on the amount of CO adsorbed and on the dispersity is shown in Fig. 2.

TABLE 3

Amount of CO adsorbed and metal dispersity of Ir/Al_2O_3 with different Ir contents

Catalyst [a]	Sample weight (mg)	CO adsorbed		Ir content (%)	S_{Ir} (m^2/g.Ir)	$\bar{d}$ (Å)
		(mg)	(mg/mg.cat)			
B-151	63.20	0.67	0.0106	8	370.50	7.23
B-152	64.85	0.71	0.0109	16.8	182.21	14.71
B-150	71.04	0.69	0.0097	30.3	89.63	29.90

[a] Reduced at 400 °C.

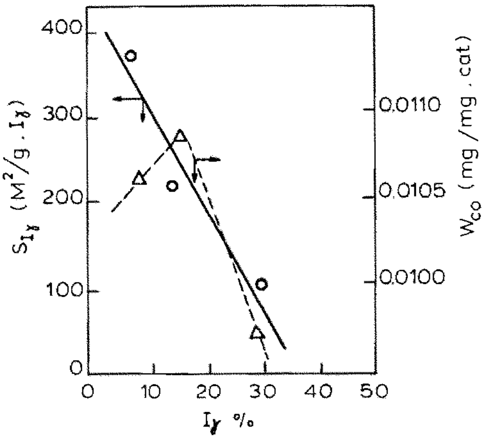

Fig. 2. Dependence of dispersity on Ir content of Ir/Al_2O_3 catalysts. O, Ni, Δ, H_2.

The results show that CO adsorption increases with increasing Ir content, and the CO adsorption per unit weight of the catalyst decreases with increasing Ir content when the Ir content is higher than 17%. Moreover, the active surface area of metal decreases and the grain size of metal increases with increasing Ir content. Thus, in the range 8–30% Ir, the dispersity decreases with increasing Ir content.

Effect of reducing temperature on dispersity

The reducing temperature of the catalyst significantly affects the dispersity of the metal. The active surface area and the average grain size of metal for catalyst B reduced at different temperatures were determined by thermogravimetry and the results are shown in Table 4 and Fig. 3. It can be seen that an increase in the reduction temperature of the catalyst leads to a decrease in active surface area and an increase in the grain size of metal, i.e. the dispersity of the metal decreases. It is possible that some iridium is sintered as the reduction temperature is increased.

TABLE 4

Amount of CO adsorbed and metal dispersity of Ir/Al_2O_3 reduced at different temperatures

Catalyst [a]	Sample weight (mg)	Reducing temperature (°C)	CO adsorbed		S_{Ir} (m^2/g.Ir)	$\bar{d}$ (Å)
			(mg)	(mg/mg.cat)		
B-150	71.32	200	0.78	0.011	100.9	26.56
B-150	71.04	400	0.69	0.010	89.63	29.90
B-150	65.43	600	0.59	0.009	83.21	32.21

[a] Ir content 30%.

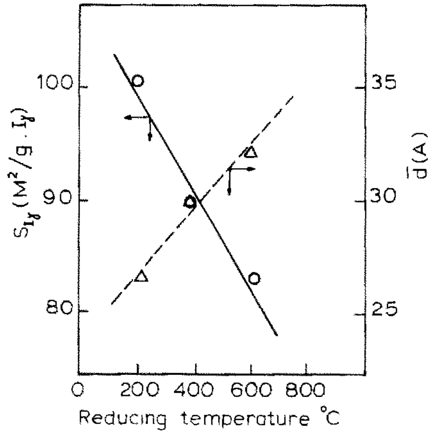

Fig. 3. Dependence of dispersity of Ir of Ir/Al_2O_3 catalyst on reduction temperature. O, N_2; Δ H_2.

Effect of different atmospheres and operation temperatures on dispersity

The dispersity of metal on the catalyst can be changed by the operation conditions. The active surface area and the average grain size of metal of catalyst C exposed to N_2 and H_2 atmospheres at different temperatures for 1 hour were determined by thermogravimetry and the results are listed in Tables 5 and 6 respectively. The relation between the dispersity and temperature in different atmospheres is shown in Fig. 4. The dispersity of Ir on the

TABLE 5

Amount of CO adsorbed and metal dispersity of Ir/Al_2O_3 at different temperatures in N_2

Catalyst	Sample weight (mg)	Operation temperature (°C)	CO adsorbed		S_{Ir}	$\bar{d}$
			(mg)	(mg/mg.cat)	(m²/g.Ir)	(Å)
C	75.71	400	1.15	0.015	167.4	16.0
C	69.85	600	0.44	0.006	69.1	38.8
C	71.90	800	0.29	0.004	44.2	60.6

TABLE 6

Amount of CO adsorbed and metal dispersity of Ir/Al_2O_3 at different temperatures in H_2

Catalyst	Sample weight (mg)	Operation temperature (°C)	CO adsorbed		S_{Ir}	$\bar{d}$
			(mg)	(mg/mg.cat)	(m²/g.Ir)	(Å)
C	66.70	400	0.67	0.010	110.9	24.2
C	66.40	600	0.94	0.014	90.8	29.5
C	65.45	800	0.52	0.008	87.1	330.7

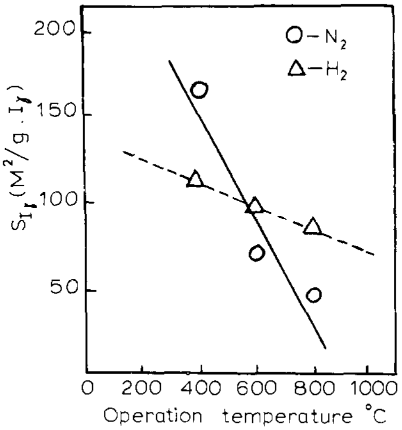

Fig. 4. Dependence of Ir dispersity of Ir/Al_2O_3 catalysts on operation temperature.

catalyst gradually decreases with increasing temperature in both N_2 and H_2. At 400 ° C, the dispersity of iridium is better under N_2 than under H_2; when the temperature exceeds 600 ° C, the dispersity under N_2 is inferior to that under H_2. As a general trend, the dispersity of Ir in N_2 decreases rapidly with increasing temperature. This demonstrates that at high temperatures the catalyst readily maintains a good dispersity of metal under a reducing atmosphere.

CONCLUSION

The metal dispersity of Ir/Al_2O_3 catalysts determined by thermogravimetry is of the same magnitude as that determined by chromatography, and the effect of reducing temperature on dispersity is observed in both cases; therefore, the metal dispersity determined by the thermogravimetric method is reliable for comparative analysis. The results show that the metal dispersity of Ir/Al_2O_3 catalysts decreases with increasing iridium content and reducing temperature. At higher temperatures, the dispersion of metal is readily maintained in a reducing atmosphere.

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