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CO–H_2 Titration for the Determination of Super Small Metal Surface Area

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A novel method is proposed for the determination of super small metal surface areas of supported metal catalysts. The method gives the amount of adsorbed CO by detecting CH_4 formed during the titration of preadsorbed CO with H_2 at elevated temperatures. The method was verified by using 0.1% and 0.5% Pt/Al_2O_3 catalysts which could be characterized by other methods. It was shown that the experimental procedure satisfies the assumptions on which the method is based and that the dispersions of both catalysts determined by the proposed method agree well with those obtained by other methods. Then the method was applied to Pt/Al_2O_3 catalysts with very low Pt content (to 0.0007%, 7 ppm), and the optimum experimental condition was established for super low metal content. The dispersions thus determined were reasonable, in the range from 80 to 100%, supporting the validity of the method.

INTRODUCTION

Determinations of the metal surface area, or the dispersion, is essential for understanding the properties of supported metal catalysts. It is usually determined by X-ray diffraction (XRD), transmission electron microscopy (TEM), and selective chemisorption (*1*). The conventional XRD method gives the average size of metal crystallites, but its application is limited to catalysts with relatively high metal content and relatively large metal crystallites. The TEM method, which gives the distribution of crystallite size directly, can be applied to catalysts with lower metal content and smaller metal crystallites than those determined by XRD. However, TEM cannot be applied to highly dispersed metal, i.e., very small metal crystallites. The selective chemisorption method is the most sensitive and is applicable to any highly dispersed catalyst. However, even the selective chemisorption method seems useless for determining very small metal surface areas because very small differences in the amounts of adsorbate gas between the beginning and end of adsorption must be detected.

Such small metal surface areas may be encountered, for example, in highly sintered catalysts which are frequently observed in catalytic combustion and in the emission control of motor vehicles. Another example is the catalyst with super low metal content. In the emission control of motor vehicles, precious metal content is sometimes as low as 0.1 g/dm^3 (ca. 0.01%). A catalyst with a metal content as low as 0.002% (20 ppm) has appeared in the literature (*2*).

In the present study, a novel method which gives the amount of adsorbed CO by detecting CH_4 formed during the titration of preadsorbed CO with H_2 has been developed for the determination of the dispersion of supported metal catalysts with very low metal surface area, and it has been applied to Pt/Al_2O_3 catalysts with a Pt content as low as 0.0007% (7 ppm). In the present method, high accuracy and high sensitivity can be expected, because the amount of formed CH_4, but not the difference, is measured with a flame ionization detector having high sensitivity.

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EXPERIMENTAL

Figure 1 shows a schematic diagram of experimental apparatus. A small amount of catalyst packed in Pyrex glass tubing was calcined in a flow of dry O_2 for 1 h at 400°C and reduced in a flow of H_2 for 1 h at 400°C after the purge of O_2 with flowing He. The catalyst was then cooled to room temperature in flowing H_2. A large pulse of CO was injected onto the catalyst through H_2 carrier gas so that the whole metal surface area could be covered by adsorbed CO. After the purge of excess CO with flowing H_2, three-way ball valves were adjusted so as to trap the adsorbed CO together with gaseous H_2. The catalyst was then heated with a preheated furnace to hydrogenate the adsorbed CO to form CH_4. After the reaction had proceeded for a predetermined time, the CH_4 formed was released by adjusting the three-way ball valves to allow detection by a frame ionization detector. A thermal conductivity detector was used for the measurement of the amount of adsorbed CO by the CO-pulse method (*3*).

The standard experimental conditions were as follows: the amount of catalyst was 0.1 g, the flow rate of gases was 40 cm^3/min, the pulse size of CO was 4 cm^3, the time for purging excess CO was 15 min, and the temperature and the time for the hydrogenation of preadsorbed CO were 400°C for 30 min or 275°C for 2 h.

High-purity CO (>99.99%) was used as received. H_2 and He were purified by passing them through a silica gel trap at liquid nitrogen temperature. O_2 was desiccated by passing it through a molecular sieve 13X column.

The catalysts were Al_2O_3-supported Pt catalysts with Pt content of 0.5% to 0.0007% (7 ppm). A 0.5% Pt/Al_2O_3 catalyst was a reference catalyst (JRC-A1-0.5 Pt) of the Catalysis Society of Japan (*3*, *4*). A reference Al_2O_3 (JRC-ALO-1) was used as the support in this case. The other catalysts were prepared by impregnating an Al_2O_3 support (another reference Al_2O_3, JRC-ALO-4) with an aqueous solution of H_2PtCl_6 containing a predetermined amount of Pt, followed by drying at 110°C overnight, calcination at 400°C for 3 h, and reduction with H_2 at 300°C for 3 h. Pt content was confirmed by using ICP (inductively coupled plasma) emission spectrophotometry (Shimadzu, GEW-170P).

RESULTS AND DISCUSSION

Verification of the Method

The present method is based on the assumptions that CO is selectively adsorbed to form a monolayer on metal surfaces but is not adsorbed on support surfaces and that all of the adsorbed CO is hydrogenated to form CH_4 selectively. The first assumption is identical to that in the conventional CO chemisorption method for the determination of metal dispersion and is widely accepted. A remaining requirement to satisfy the first assumption is that enough CO is introduced to cover all the metal surface. The pulse size of CO under the standard

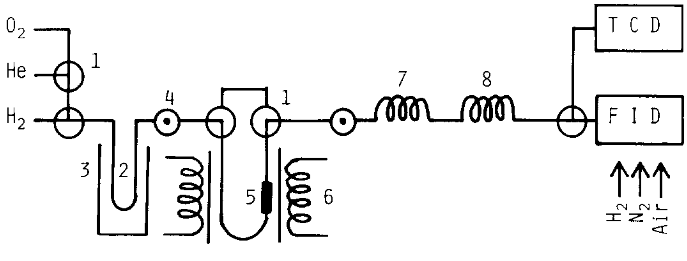

FIG. 1. Schematic diagram of apparatus of CO–H_2 titration. (1) Three-way ball valve; (2) silica gel trap; (3) liquid nitrogen bath; (4) pulse inlet; (5) catalyst; (6) furnace; (7) celite column; and (8) molecular sieve 13X column.

condition mentioned above seems to meet the requirement. This is because the pulse size of 4 cm^3 is about 70 times larger than the charged amount of Pt in the case of the 0.5% Pt/Al_2O_3 catalyst, which has the highest Pt content among the catalysts examined in the present study. By way of precaution, the effect of pulse size was examined by using 0.5% Pt/Al_2O_3. As shown in Fig. 2, the pulse size did not have any effect in the range 1 to 8 cm^3. The amount of CH_4 formed did not change at all when two or three pulses of 2 cm^3 were introduced successively. Thus, it has been shown that the requirement for the first assumption is satisfied. The verification of the second assumption, which is peculiar to the present method, will be shown below.

Al_2O_3 support. In order to confirm the inactivity of the Al_2O_3 support toward the formation of CH_4, preliminary runs were conducted under the abovementioned condition using 0.5 g of Al_2O_3 supports (JRC-ALO-1 and JRC-ALO-4). This was to prevent contaminants on the Al_2O_3 surface from being hydrogenated to form CH_4, although it is widely accepted that CO is not adsorbed on the Al_2O_3 surface. As a result of the runs, it was confirmed that both Al_2O_3 supports produced only negligible amounts of CH_4 even in the reaction at 400°C for 30 min.

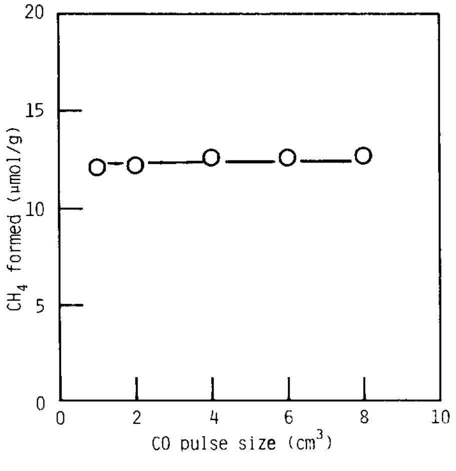

FIG. 2. Effect of CO pulse size on the amount of CH_4 formed on the 0.5% Pt/Al_2O_3 catalyst at 400°C for 30 min.

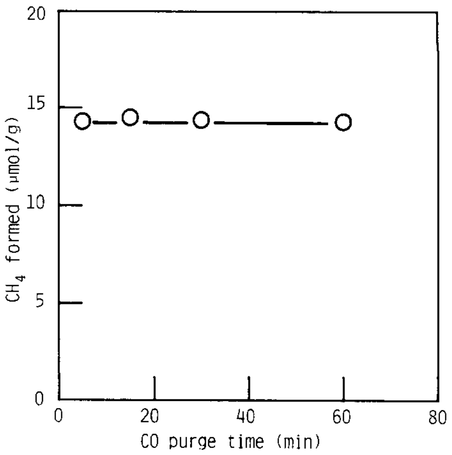

FIG. 3. Effect of purging time on the amount of CH_4 formed on the 0.5% Pt/Al_2O_3 catalyst at 400°C for 30 min.

0.5% Pt/Al_2O_3. For the verification of the abovementioned assumption, the method was applied to the 0.5% Pt/Al_2O_3, the dispersion of which can also be measured by the other methods because of its moderately large Pt surface area.

The selective formation of CH_4 was confirmed by using a Porapak Q column in place of the molecular sieve 13X column. No hydrocarbons other than CH_4 were detected, which seems quite reasonable because of the very high H_2/CO ratio.

The requirement that only adsorbed CO is to be hydrogenated can be easily fulfilled by a thorough purge of excess CO. As shown in Fig. 3, the purging time did not have any effect above 5 min, indicating that excess CO can be thoroughly purged under the standard purging time of 15 min. It should be added that the amount of CH_4 formed that was measured after the thorough purge corresponds to that of irreversibly adsorbed CO.

The final requirement that all of the adsorbed CO is to be hydrogenated may depend on both the reaction temperature and the reaction time. The open circles in Fig. 4 show the effect of the reaction temperature

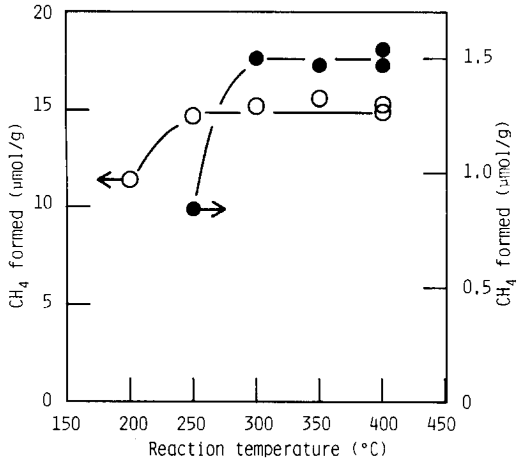

FIG. 4. Effect of reaction temperature on the amount of CH_4 formed on the 0.5% (○) and 0.1% (●) Pt/Al_2O_3 catalysts at 30 min.

on the amount of CH_4 formed. Although the amount of CH_4 increased with increasing temperature from 200 to 250°C, it was essentially constant above 250°C.

Figure 5 shows the effect of reaction time. At 400°C, as shown by the open circles, the amount of CH_4 formed did not depend on the reaction time in the range 5 to 30 min. However, at 250°C, the amount of CH_4 formed was constant only after the reaction had proceeded for longer than 10 min, indicating that a longer reaction time is necessary at lower temperature. It was confirmed by using TCD in place of FID that under these conditions no CO was released from the catalyst bed without being hydrogenated. It should be noted that the scatter in the amount of CH_4 formed from series to series, such as the difference in the constant value between 250 and 400°C in Fig. 5, is due to sintering caused by repeated pretreatment, as reported elsewhere (*5*).

Table 1 shows the dispersion calculated from the amount of CH_4 formed on the assumption that $CH_4/Pt_s = 1$. The table also includes the reported dispersion of the catalyst (*5*, *6*) for comparison. Since, as mentioned above, the amount of CH_4 formed corresponds to that of irreversibly adsorbed CO, the amounts of irreversibly adsorbed species are cited for the static adsorption of H_2 and CO. As shown, the results of the present method agree well with those obtained by other methods within the above-mentioned scatter.

TABLE 1

Dispersion of 0.5% Pt/Al_2O_3 Catalyst (JRC-Al-0.5 Pt)

Method		Dispersion	Ref.
A. $CO-H_2$ titration	CO/Pt	0.58	This study
B. $CO-H_2$ titration	CO/Pt	0.66–0.45[a]	This study
C. Pulse adsorption	CO/Pt	0.54[b]	This study
D. Pulse adsorption	CO/Pt	0.71–0.54[a]	This study
E. Pusle adsorption	CO/Pt	0.80–0.33[a]	(*5*)
F. Static adsorption	CO/Pt	0.62[c]	(*6*)
G. Static adsorption	O/Pt	0.55	(*6*)
H. Static adsorption	H/Pt	0.84[c]	(*6*)

[a] The scatters are mainly due to slow sintering (see text).

[b] Measured immediately after run A.

[c] Irreversibly adsorbed amount.

Row C in Table 1 shows the dispersion determined from the CO pulse adsorption which was conducted immediately after the $CO-H_2$ titration run (row A) in order to minimumize the effect of sintering. As shown, the results are in good agreement with each other, indicating the validity of the present method.

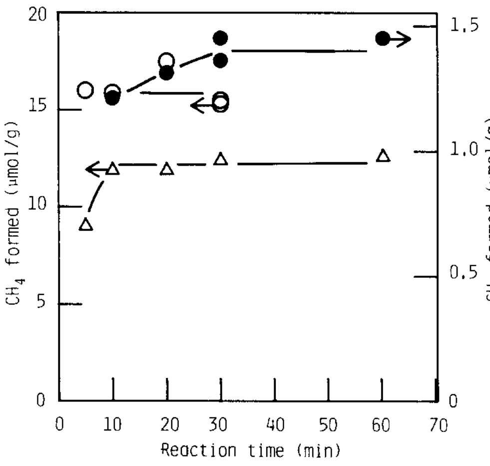

FIG. 5. Effect of reaction time on the amount of CH_4 formed on the 0.5% Pt/Al_2O_3 at 400°C (○) and at 250°C (△) and on 0.1% Pt/Al_2O_3 at 300°C (●).

0.1% Pt/Al_2O_3. CO–H_2 titration was applied to the 0.1% Pt/Al_2O_3 catalyst for further verification. The results are shown by the solid circles in Figs. 4 and 5. As shown in Fig. 4, the effect of reaction temperature on the present catalyst was different from that on the 0.5% Pt/Al_2O_3 catalyst. The amount of CH_4 formed on the present catalyst was constant only above 300°C, while it was constant above 250°C on the 0.5% Pt/Al_2O_3 catalyst. This indicates that higher temperature is necessary for the 0.1% Pt/Al_2O_3 catalyst because of lower metal content. Figure 5 indicates that a longer reaction time is also necessary for the present catalyst. As shown, the amount of CH_4 was constant only after reaction times longer than 30 min at 300°C, while it attained a constant value after 10 min even at 250°C on the 0.5% Pt/Al_2O_3. These results indicate that the dispersion of the present catalyst can be measured by conducting the reaction at 300°C for 30 min.

Table 2 summarizes the dispersions measured under the abovementioned condition by using various amounts of catalyst as well as those measured under various conditions. As shown, the CO–H_2 titration gave an essentially constant value of the dispersion independent of the amount of catalyst used and of the reaction temperature. The table also includes the dispersion determined by the CO pulse adsorption conducted for comparison by using a relatively large amount of catalyst. The dispersion measured by the CO pulse method agreed well with that obtained by CO–H_2 titration, indicating the validity of the method.

TABLE 2

Dispersion of 0.1% Pt/Al_2O_3 Catalyst

Method	Catalyst weight (g)	Reaction temperature (°C)	Reaction time (min)	Dispersion
CO–H_2 titration	0.05	300	30	0.25
	0.1	300	30	0.24
	0.5	300	30	0.23
	0.5	400	30	0.24
	0.5	400	60	0.24
	0.1	275	120	0.26
CO pulse adsorption	0.5	—	—	0.26

Application to Catalysts with Super Low Pt Content

The application of CO–H_2 titration to the 0.007% Pt/Al_2O_3 catalyst gave a strange result; that is, the amount of CH_4 formed at 400°C for 30 min corresponded to the dispersion of 1.86. When the amount of CH_4 formed on the Al_2O_3 support (JRC-ALO-4) was again measured carefully under the same conditions, the amount corresponded to the dispersion of only 0.01 for the 0.007% Pt/Al_2O_3 catalyst. Next, a blank run was conducted to examine the formation of CH_4 on the catalyst without preadsorbed CO, and it was found that a significant amount of CH_4 was formed even after several blank runs. Probably contaminants on the Al_2O_3 surface migrate onto the Pt surface and are hydrogenated to form CH_4. Since it was reported that the reference Al_2O_3 adsorbs a significant amount of CO_2 (7), CO_2 adsorbed on the Al_2O_3 surface may be the most probable source of CH_4 formed in the blank run.

It should be noted that significant amounts of CH_4 were formed in the blank run on the catalysts with very low Pt content, but only negligible amounts of CH_4 were formed on the 0.1 and 0.5% Pt/Al_2O_3 catalysts. In the latter, the contaminants may be almost completely hydrogenated on the Pt surface and removed during pretreatment. On the other hand, in the case of the catalysts with very low Pt content, only a portion of contaminants may be hydrogenated during pretreatment because of low catalytic activity due to low Pt content, and the residual contaminants may be hydrogenated to CH_4 in the blank run. In the case of the Al_2O_3 supports, as mentioned above, only negligible amounts of CH_4 were produced even in the pretreatment. This may be because the contaminants cannot be hydrogenated because of the very poor activity of Al_2O_3 for hydrogenation.

Although prolonged pretreatment at higher temperature might be effective in removing the contaminants, it may also lead to sintering. Thus, an attempt was made to lower the reaction temperature so that CH_4 could not be formed in the blank run. On the catalysts containing 0.007, 0.006, and 0.0007% Pt, the amounts of CH_4 formed were negligible in the blank runs at 275°C, although a slight amount of CH_4 was formed at 300°C.

Figure 6 shows the effect of the reaction time on the amount of CH_4 formed over 0.007% (70 ppm) and 0.0007% (7 ppm) Pt/Al_2O_3 catalysts at 275°C. As shown, the amounts were constant on both catalysts at reaction times longer than 2 h. A series of runs was done for 0.0007% Pt/Al_2O_3 at 250°C to confirm the results at 275°C. As shown by the triangles in Fig. 6, the amount of CH_4 formed at reaction times longer than 6 h attained a constant value, which agrees well with the data at 275°C.

The longer reaction times required for these catalysts may result not only from very small Pt content but also from low activity of individual surface Pt atoms. The activity of individual surface Pt atoms is expected to be lower on the catalysts with very low Pt content than that on the conventional Pt/Al_2O_3 catalyst. This is because CO hydrogenation is a structure-sensitive reaction requiring a quite large metal ensemble (*8*) and because low Pt content is expected to result in high dispersion, i.e., a small ensemble of Pt. Further, it may be possible that partially oxidized Pt is responsible for lower specific activity. It has been reported (*9*) that diffuse reflectance FT–IR spectra of adsorbed CO on these catalysts exhibit an IR band at 2140 cm^{-1}, which has been assigned to adsorbed CO on oxidized Pt (*10*).

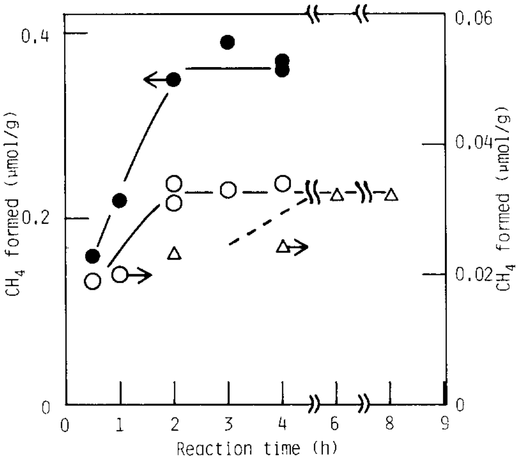

FIG. 6. Effect of reaction time on the amount of CH_4 formed on the 0.0007% (7 ppm) Pt/Al_2O_3 at 275°C (○) and at 250°C (△) and on 0.007% (70 ppm) Pt/Al_2O_3 at 275°C (●).

TABLE 3

Dispersion of Pt/Al_2O_3 catalysts with Super Low Pt Content

Pt content (wt%)	CH_4 formed (μmol/g)	Dispersion
0.028 (280 ppm)	1.16	0.81
0.007 (70 ppm)	0.35	0.98
0.006 (60 ppm)	0.25	0.81
0.0007 (7 ppm)	0.034	0.95

Table 3 summarizes the dispersions of the catalysts with very low Pt content thus determined through the CO–H_2 titration at 275°C for 2 h. The results could not be verified by other methods because the dispersion of such small amounts of Pt cannot be measured by any other method. But it may be said that the high dispersion obtained for very low Pt contents suggests the validity of the results, because lower Pt content is expected to result in higher dispersion.

CONCLUSION

A CO–H_2 titration method has been proposed for the determination of super small metal surface areas. It was shown that the dispersion of Pt/Al_2O_3 catalysts with super low Pt content (to 0.0007%, 7 ppm) can be measured under the following conditions: the catalyst weight is 0.1 g, the pulse size of CO is 4 cm^3, and the reaction temperature and time for the hydrogenation of preadsorbed CO are 275°C for 2 h.

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