JOURNAL OF CATALYSIS **86**, 446–449 (1984)

Influence of Water in the Reduction Stage of Oxygen-Adsorbed Platinum Supported on γ-Alumina

Many methods are recommended for measurement of the number of active sites on a metallic catalyst surface, however, the CO pulse technique is most often used as a convenient and accurate method (*1*). Although there are many merits in this method, some problems still remain (*2, 3*). One of the most important problems is the effect of the pretreatment of a catalyst before the CO adsorption, in particular the reducing conditions. It is known that existing water during the heating and/or reducing processes plays an important role on the nature of the metal oxide catalyst (*4–8*), however, quantitative estimation has not been studied extensively. The work reported here was undertaken to study the reduction conditions of an alumina-supported platinum catalyst in the oxidized state. Reduction conditions were varied and then the influence on the metal dispersion was estimated quantitatively by CO uptake, and the effect of water was discussed.

The catalyst was supplied by the Catalysis Society of Japan as JRC-Al-0.5Pt (0.5% Pt/Al_2O_3). It was prepared by impregnating γ-alumina (60–200 mesh, 177 m^2/g, precalcined at 700°C) with chloroplatinic acid solution. The impregnates were dried overnight at 110°C, and oxidized at 450°C and then reduced in H_2 at 300°C. The content of Pt was 0.5 wt%.

To measure CO uptake the flow system was connected to a thermal conductivity detector and used under atmospheric pressure. Reduction in a H_2 flow was carried out *in situ* as follows. The catalyst sample of about 0.1 g was packed in a Pyrex tube (3.5 mm i.d.). There, helium was introduced as a carrier gas at a flow rate of 40 cm^3/min for more than 1 h. Hydrogen of about 4.5 cm^3/min was then added into the He stream, and in this way H_2 concentration was controlled to about 10%. The temperature was raised at a constant heating rate of 10°C/min from room temperature to 450°C, and maintained for 10 min at this temperature. The elution of residual hydrogen was carried out with He for 5 min at the same temperature. After the system was cooled to 25°C, CO pulse of 25 μl was injected repeatedly just in front of the catalyst bed using a microsyringe until no more irreversible adsorption could be observed. Substantial irreversible CO uptake was calculated from the obtained chromatogram. A four–nine grade He, a seven–nine grade H_2, and a research grade CO were used.

When measuring the volume of adsorbed gases, great attention has been paid to not only the pretreatment, for example, reduction in H_2, but also the measuring conditions (*9–11*). First of all, therefore, we confirmed the following points.

(i) Further purification of the carrier gas: In order to remove possible impurities, such as H_2O and O_2 in the carrier gas (He), an MS-5A (60–80 mesh, 60 cm^3) trap immersed in the liquid N_2 and a deoxygenator packed with a copper catalyst at 350°C were employed. However, this experiment gave the same CO uptake within the measurement accuracy as the experiment without any purification.

(ii) Elution of retained hydrogen species: The elution conditions, even cooling to room temperature in 10% H_2, had no effect on the subsequent CO adsorption. This indicates that CO is much more strongly ad-

0021-9517/84 $3.00

sorbed on Pt than hydrogen; consequently CO will be adsorbed from a flowing gas stream at room temperature, and any adsorbed hydrogen on the Pt surface will be readily desorbed.

(iii) Pulse volume of injected CO: If the pulse volume is too small, an experimental error may accumulate because of the delay in attaining an adsorption equilibrium. From preliminary experiments, it was clear that about 40 μl of CO was necessary to saturate the active sites of a 0.1-g portion of the catalyst, and then the pulse volume was changed by three steps, 25, 50, and 100 μl. However, no change in CO uptake was observed.

(iv) Quantity of the catalyst used: A smaller quantity of the catalyst used may also give rise to an experimental error, because the absolute adsorption-volume would be small. The catalyst weight was changed from 0.1 to 0.4 g, but no difference was shown.

In these investigations, adsorption measurements were carried out 12 times, and CO uptakes coincided at a value of 0.417 ± 0.017 cm^3/g-catalyst or 83.8 cm^3/g-Pt, and a metal surface area 293 m^3/g-Pt (*12*), average size of Pt particle 9.6 Å, and dispersion 0.73.

Factors that affected the result of adsorption were then investigated.

The gas flow rate in H_2 reduction: Figure 1 shows the effect of the gas-flow rate on CO uptake. The CO uptake changed little with the total gas (He + H_2) flow rate above ca. 40 cm^3/min, however, it decreased drastically with a flow rate below ca. 20 cm^3/min. The change in the flow rate can lead to the change in the contact time of the H_2O formed on the catalyst surface. The lower flow rate results in a longer contact time, and therefore the water formed might have an influence on the situation of hydrogen on the catalyst surface.

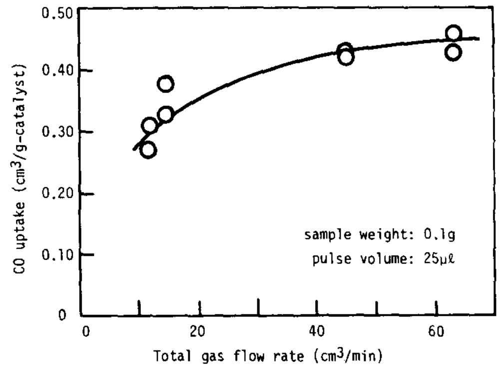

FIG. 1. Influence of total gas-flow rate in H_2-reduction on CO uptake.

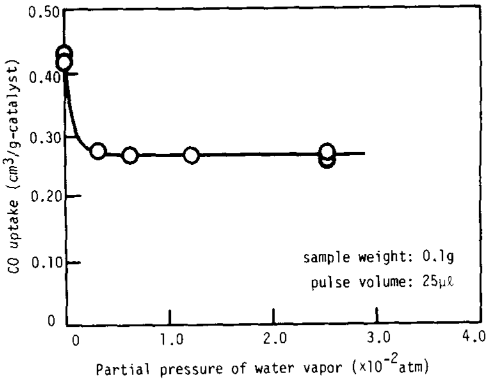

FIG. 2. Influence of added water vapor in H_2-reduction stage on CO uptake.

Influence of added water. Since CO uptake seems to be affected by existing H_2O formed as mentioned above, H_2O was added intentionally at the reducing step with varying the partial pressure. As shown in Fig. 2, the CO uptake drastically decreased from 0.42 to 0.26 cm^3/g-catalyst by addition of only 0.003 atm H_2O. For above this partial pressure, the CO uptake consistently showed the value of 0.26 cm^3/g-catalyst. After the catalyst decreased its CO uptake to this lower value, it was treated repeatedly according to the standard procedure without H_2O addition, and the decreased CO uptake was reproduced. This indicates that the water added accelerates both the rate of H_2 adsorption on the metal nuclei and the hydrogen spillover to the metal oxide part, resulting in a rapid hydrogen reduction accompanying sintering of Pt crystallites due to the concentrated reaction heat.

In Table 1, the CO uptakes (cm^3/g-cata-

TABLE I

CO Uptakes by Various Pretreatments

Exp.	Pretreatment condition	CO uptake (cm^3/g-catalyst)
1	Heating in 10% H_2/He stream from room temperature to 450°C	0.42
2	Coexistence of H_2O vapor (0.012 atm) and H_2 at room temperature for 4 min, followed by elution with He stream for 0, 2, and 7 h	0.26
3	Contact with H_2O vapor (0.012 atm) at room temperature and heating in He stream	0.26–0.36
4	Oxidized at 300°C for 30 min in an air stream	0.0

lyst) for various pretreatments are summarized. Experiment 1 was by the standard procedure and gave a CO uptake of 0.42. Experiment 2 shows the result of coexistence of H_2O vapor and H_2 at room temperature. The value of 0.26 was consistently given irrespective of the elution time before heating or reduction, and agrees with the value when H_2O vapor was added to the H_2-reduction stage. This indicates that the existence of H_2O accelerates hydrogen spillover, and even at room temperature the reduction of the oxidized platinum surface can easily occur accompanying sintering. The value of 0.26 seems to correspond to a limit of sintering. The reason is considered to be as follows. Platinum particles dispersed originally would fairly easily gather or grow to larger particles by sintering. However, the larger particles thus produced cannot gather or grow any more by moderate reduction conditions due to a geometric hindrance of the support surface or a stable shape of platinum particles such as a sphere. Experiment 3 was the case of contact with merely H_2O vapor at room temperature followed by heating to 450°C in He for 1 or 3 h. The values of CO uptakes 0.345 ± 0.015 were obtained in these cases. It was confirmed that the oxidized sample had no CO uptake (Exp. 4). These suggest that H_2O strongly adsorbed on the catalyst surface and partially oxidized the metallic part.

Benson *et al.* (*6*) reported that WO_3 mixed with platinum black could be reduced at about 100°C, while if there existed adsorbed water, the reduction could take place rapidly even at room temperautre. This observation can be the support for the above-mentioned consideration. Furthermore, in order to confirm the low-temperature reduction, H_2 consumption during the reduction was measured by temperature-programmed reduction (TPR) by gas chromatography. The apparatus was modified by addition of a Dryice-methanol trap to remove the produced water between the sample cell and the gas chromatograph. Argon instead of He was used as a carrier gas. A catalyst oxidized in air for 10 min at 300°C was used. The concentration of H_2 could not exceed 0.5% because of the limitation of the sensitivity of the gas chromatograph, and in this concentration range no difference in CO uptake was obtained with or without addition of water vapor. Each chromatogram showed almost the same broad peaks showing the slow consumption of H_2 ranging from 210 to 350°C. The low H_2 concentration must have led a low reduction rate and have given no sintering.

To elucidate the role of water, Hopcalite from Nakarai Chemicals Company Ltd. was employed as a model sample. It has a high activity for CO oxidation at low temperatures like as platinum catalysts. It was composed of 5% Ag_2O, 30% CuO, 15% Co_2O_3, and 50% MnO_2, and some part of the oxides could easily be reduced by H_2 or CO. Since the amount of H_2 consumption during the course of reduction was large, an evident gas chromatographic reflection was expected. Figure 3 shows the effect of wa-

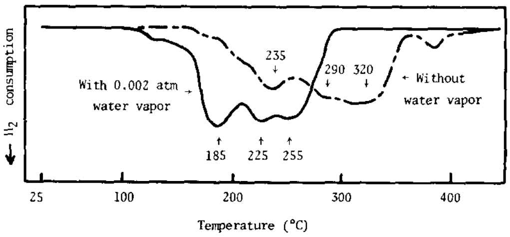

FIG. 3. Temperature-programmed H_2-reduction of Hopcalite.

ter vapor on the TPR profile. Although there are multiple peaks due to the mixed oxides, by the addition of water vapor the TPR profile shifted ca. 60°C to a lower temperature and its sharpness increased. This supports the contention that H_2O plays the role of accelerating hydrogen spillover.

In conclusion, the amount of CO uptake of the highly dispersed Pt catalyst supported on γ-alumina is affected by the presence of water on the catalyst surface during the course of prereduction treatment. Therefore, when the linear velocity of the reduction gas is too small such as 1 cm/s, the produced water by H_2 reduction can be in contact with the catalyst surface, and accelerates the hydrogen spillover and causes sintering of supported platinum.

ACKNOWLEDGMENTS

We thank the Catalysis Society of Japan for providing the catalyst. We also give thanks for the referee's invaluable comment concerning the effect of elution conditions.

REFERENCES

1. Whyte, J. T. E., *Catal. Rev.* **8,** 117 (1973).

2. Arai, H., and Tominaga, H., *J. Catal.* **43,** 131 (1976).

3. Yates, D. J. C., Murrell, L. L., and Prestridge, E. B., *J. Catal.* **57,** 41 (1979).

4. PB Report 97368 (1949).

5. Uchida, M., Arai, H., and Tominaga, H., *Shokubai (Catalyst)* **22**(4), 310 (1980).

6. Benson, J. E., Kohn, H. W., and Boudart, M., *J. Catal.* **5,** 307 (1966).

7. Glassl, H., Kramer, R., and Hayek, K., *J. Catal.* **63,** 167 (1980).

8. Zakumbaeva, G. D., Omashev, Kh. G., and Kham, Ch., *React. Kinet. Catal. Lett.* **6**(3), 363 (1977).

9. Scholten, J. J. F., and Montfoort, A. Van., *J. Catal.* **1,** 85 (1962).

10. Hausen, A., and Gruber, H. L., *J. Catal.* **9,** 125 (1967).

11. Carballo, L., Serrano, C., Wolf, E. E., and Carberry, J. J., *J. Catal.* **52,** 507 (1978).

12. Kokes, R. J., and Emmett, P. H., *J. Amer. Chem. Soc.* **82,** 1037 (1960).

TOMOYUKI INUI
TAKANORI MIYAKE

Department of Hydrocarbon Chemistry
Faculty of Engineering, Kyoto University
Sakyo-ku, Kyoto 606, Japan

Received May 17, 1983; revised October 27, 1983