Adsorbed CO on Pt/Al$_2$O$_3$ with Super Low Pt Content in CO–H$_2$ Titration: Reply to Bozon-Verduraz *et al.*

In a recent letter to the editor, Bozon-Verduraz *et al.* (*1*) raised a few questions about a novel method, CO–H$_2$ titration, for the determination of super small metal surface area proposed by us (*2*). The method is characterized by high sensitivity and accuracy, because, in the method, the amount of CH$_4$ formed through the hydrogenation of preadsorbed CO is measured with a flame ionization detector having high sensitivity. Actually, the dispersions of Pt/Al$_2$O$_3$ catalysts with super low Pt content down to 0.0007% (7 ppm) have been successfully measured by the method.

The amount of formed CH$_4$ is measured in the following procedures: (1) A large pulse of CO is injected onto a prereduced catalyst through H$_2$ carrier gas at room temperature, and excess CO is purged by flowing H$_2$. (2) The adsorbed CO is trapped together with gaseous H$_2$ in a U-tube reactor. (3) The catalyst is heated to hydrogenate the adsorbed CO to form CH$_4$. (4) The formed CH$_4$ is released for the detection by a flame ionization detector.

This method is based on the assumptions that CO is selectively adsorbed to form a monolayer on metal surface but not on support surface, and that all of the adsorbed CO is hydrogenated to form CH$_4$ selectively.

The questions raised by Bozon-Verduraz *et al.* (*1*) are related to the first assumption, which is not particular to the present method, but is common to all the selective chemisorption methods for the determination of metal surface area (*3*).

The first question is about the error due to the adsorption of CO on support surface, although they confirmed that the adsorbed CO on Al$_2$O$_3$ surface is almost completely removed under the condition equivalent to that in the CO–H$_2$ titration. In very early papers (*4*), the adsorption of H$_2$ and CO on support surface, especially on highly evacuated surface, was observed, and the adsorption parameters were selected to avoid or minimize the problem. One of the attempts is a pulse adsorption of CO which gives the amount of only irreversibly adsorbed CO excluding that on the support surface (*5*).

The situation in the CO–H$_2$ titration is identical to that in the CO-pulse method: Physically adsorbed CO on the support surface can be removed through the purge with H$_2$ carrier gas. The absence of adsorbed CO on the support surface can be confirmed through IR spectra. IR spectra of adsorbed CO on Pt/Al$_2$O$_3$ catalysts used in the CO–H$_2$ titration were measured by a diffuse reflectance FT–IR spectrometer, and were reported previously (*6*). The spectra were measured under a condition similar to that in the CO–H$_2$ titration: A large pulse of CO was introduced onto a prereduced catalyst through H$_2$ carrier gas at room temperature, and IR spectra were recorded after the purge of "excess CO." Both the linear CO bound near 2060 cm^{-1} and the bridge CO band around 1800 cm^{-1} could be observed above 0.14% of Pt, but below 0.027% Pt, the bridge CO band could not be observed at a significant intensity. Below the Pt content of 0.006% (60 ppm), another band, which has been assigned to adsorbed CO on oxidized Pt ion site, was observed at 2140 cm^{-1}. However, the band assignable to adsorbed CO on Al$_2$O$_3$ surface could not be observed at 2200 cm^{-1}. Thus, it can be concluded that adsorbed CO on Al$_2$O$_3$ surface is absent or, at least, negligible under the condition of CO–H$_2$ titration.
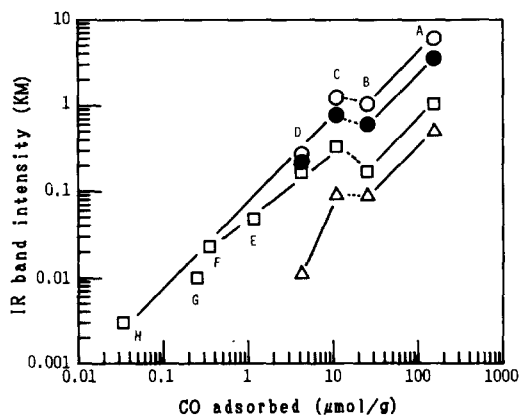
Further evidence of the validity of the

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FIG. 1. IR band intensities of linear CO (□), bridge CO (△), and the sum of them (○, ●) as a function of the amount of adsorbed CO measured by the CO-pulse method (A to D) and by CO–H₂ titration (E to H). Pt content of catalyst: A, 5% (CO/Pt = 0.6); B, 5% (CO/Pt = 0.10); C, 0.27%; D, 0.14%; E, 0.028% (280 ppm); F, 0.007% (70 ppm); G, 0.006% (60 ppm); and H, 0.0007% (7 ppm). For the sum of band intensities, see text.

method is given in Fig. 1, where IR band intensity is plotted against the amount of adsorbed CO measured by the CO-pulse method for samples A to D (7) and by the CO–H₂ titration for samples E to H. Closed and open circles represent the sum of band intensities of linear CO and bridge CO calculated by assuming the ratio of the extinction coefficient of linear CO to that of bridge CO to be 5 to 10, respectively. This assumption is based on the report that the ratio on supported Pt catalysts is in the range 4 to 13 (8). As shown, a linear correlation with a slope of unity is observed between a logarithm of total band intensity (sum of linear CO and bridge CO for samples C and D, and linear CO for samples E to H) and that of the amount of adsorbed CO without any discontinuity between samples D and E. That is, the total band intensity is proportional to the amount of adsorbed CO irrespective of the method for measuring the amount of adsorbed CO.

It should be added that the discontinuity between samples B and C may be caused by

a highly dark color of samples A and B with higher Pt content. This is because the band intensity of the Kubelka–Munk spectrum (9) in diffuse reflectance spectroscopy, which corresponds to the absorbance spectrum, depends not only on the extinction coefficient but also on a scattering constant of powder layer, and the scattering constant varies with the darkness of sample.

Bozon–Verduraz et al. also referred to strongly adsorbed CO on MgO (10), ThO₂ (11), and CeO₂ (12). However, these species were observed on highly dehydroxylated surfaces which are hardly obtained by the conventional pretreatment in the selective chemisorption methods. In the CO–H₂ titration, a catalyst is pretreated under rather mild conditions; that is, the catalyst is oxidized and reduced at 673 K, but not evacuated. The reduction temperature may be lowered if necessary: For example, in the characterization of EUROPT-1, the catalyst was reduced between 428 and 673 K for H₂ adsorption (13). Thus, it does not seem difficult to select the optimum experimental condition of the CO–H₂ titration for metal catalysts supported even on these oxides so as to satisfy the above-mentioned assumptions.

The second question is about the error due to the desorption of CO adsorbed on metal surface. The CO-pulse method is said to give the amount of irreversibly adsorbed CO (5). Actually, the amount measured by the CO-pulse method agrees well with that of irreversibly adsorbed species measured by the static method (14). This is also the case for the CO–H₂ titration. As described in our previous paper (2), the amount of formed CH₄ corresponds to that of irreversibly adsorbed CO, and agrees well with those of irreversibly adsorbed species measured by the static adsorption of H₂ and CO.

In conclusion, the interest of CO–H₂ titration for the measurement of super small metal surface area has been reinforced by the letter of Bozon-Verduraz et al. (1) and the present reply.

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