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LETTER TO THE EDITORS

States of Platinum in the Zirconium Oxide Promoted by Platinum and Sulfate Ion

In their previous note (*1*), Paál *et al.* proposed a possible state of platinum in Pt/SO_4^{2-}–ZrO_2 on the basis of the XPS data presented in our previous paper (*2*). They suggested that the state of the platinum was mostly metallic and the metallic platinum was covered with sulfur.

As Muhler *et al.* warned in their note, special care should be taken in measuring an insulator sample. We are aware of what will happen in the XPS spectra of an insulator sample. In some cases, differential charging (inhomogeneous electrostatic charging) results in unusual line broadening and deformation of the XPS peaks. In the present case, such unusual line broadening and deformation could not be observed for Zr 3*d* spectra of the support (SO_4^{2-}–ZrO_2), as shown in Fig. 1. Only a considerable charging shift of 5.9 eV was apparent, without deformation or extensive broadening. Since the platinum is supported on the SO_4^{2-}–ZrO_2, it is not plausible that the differential charging, if it exists, affects only the line shape of the supported platinum species and not the line shape of the support. Therefore, we consider that inhomogeneous electrostatic charging does not occur in the present case.

We also recognize that the XPS peak for the Pt 4*f* orbital cannot be exactly fitted by any symmetric function. However, the line shape may be fitted by a symmetric function as a first approximation. For an exact quantitative calculation for the platinum cation/metal ratio, the use of a symmetric function may not be adequate. We intended to show that metallic platinum composed a small fraction as compared to the platinum cation. The calculated values of 4.5 and 6.1 given in Table 2 of Ref. (*2*) are based on the FWHM values in the same table. If the FWHM values of 1.80 and 2.82 were used for Pt metal and Pt cation, respectively, which were estimated from the XPS peaks in Fig. 4 in our paper (*2*), the cation/metal ratios are calculated to be 3.3 instead of 6.1 for the sample prereduced at 673 K. We should have described this point in our paper. Nevertheless, it is still obvious that Pt cations predominate over metallic Pt.

Determination of the exact oxidation states for platinum is difficult, and it was not possible for the prereduced Pt/SO_4^{2-}–ZrO_2. We do not insist that platinum is in the state Pt^{4+}. We believe that the peaks of higher binding energies in our sample contain more than one component, as is described in our paper.

As Paál *et al.* suggested, the formation of PtS is possible even if a significant change in the Pt 4*f* spectrum is not observed. We have already suggested the formation of PtS when prereduced at 673 K on the basis of S 2*p* and Pt 4*f* XPS spectra (*2*). However, because of a lack of exact data for the binding energy of the compound PtS, we do not wish to rely on the XPS spectra to indicate the formation of PtS until we observe a definite spectrum ascribed to PtS.

It is likely for most of the Pt catalysts extensively investigated in the past that the reduction of the majority of the Pt occurs in hydrogen at temperatures up to 673 K. The characteristic features of the platinum in Pt/SO_4^{2-}–ZrO_2, which are presented in our papers, are different from those of usual platinum catalysts. Retention of a high oxidation state of platinum in the hydrogen stream at 673 K is certainly rare, but occurs

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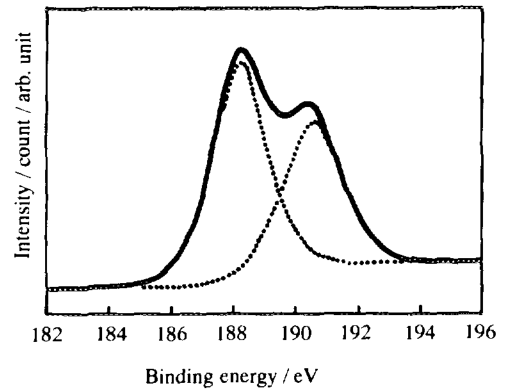

FIG. 1. Zr 3*d* XPS spectra of the Pt/SO_4^{2-}–ZrO_2 sample after hydrogen treatment at 673 K. The separation curves are shown by dotted lines. The binding energies of the abscissas are not corrected.

in the case of Pt/SO_4^{2-}–ZrO_2. This may be best shown by temperature-programmed reduction (TPR). The TPR plot for Pt/SO_4^{2-}–ZrO_2 is shown in Fig. 2, together with that of Pt/ZrO_2. As for most platinum catalysts, a hydrogen consumption peak begins to appear at about 400 K for the Pt/ZrO_2 sample. It is to be noted, however, that a hydrogen consumption peak begins to appear beyond 600 K for the Pt/SO_4^{2-}–ZrO_2 sample. The temperature difference marking the onset of reduction of platinum exceeds 200 K. The platinum in Pt/SO_4^{2-}–ZrO_2 is extremely difficult to reduce as compared to usual platinum catalysts.

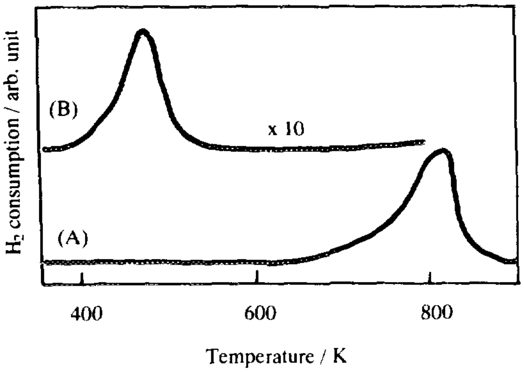

FIG. 2. Temperature-programmed reduction plots for (A) Pt/SO_4^{2-}–ZrO_2 and (B) Pt/ZrO_2.

It is, therefore, difficult to accept the ideas proposed by Paál *et al.* (*1*) that the state of the platinum in Pt/SO_4^{2-}–ZrO_2 is mostly metallic and the surface of the metallic platinum is covered with sulfur. The state of the platinum in Pt/SO_4^{2-}–ZrO_2 is mostly cationic after reduction with hydrogen at temperatures below 673 K. The platinum particles on the support are covered with sulfur to some extent after reduction at 673 K.

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