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LETTERS TO THE EDITORS

Contradictions in the Interpretation of Experimental Results Obtained upon High-Temperature Hydrogen Treatment of Supported Platinum Catalysts

In recent years growing interest has been paid to the study of the influence of high-temperature hydrogen treatment (HTHT) on the hydrogen adsorption and catalytic properties of the supported Pt catalysts (*1–4*).

Recently Kunimori *et al.* (*5*) have proposed a plausible redox reaction (see below) on the basis of the correlation found between the decrease (or increase) in the amount of H_2 chemisorption (ΔH/Pt) and the amount of H_2 (or O_2) consumptions during the pretreatment processes.

$$Pt + Al_2O_3 \underset{0.5O_2,\ 400^\circ C\ (b)}{\overset{H_2,\ 500^\circ C\ (a)}{\rightleftarrows}} Pt \cdot Al_2O_2 \quad (1)$$

More recently this approach has been extended to study the SMSI behavior of the Pt/TiO_2 catalyst (*6*).

We have found certain contradictions in works (*4–6*) and the aim of our comment is to demonstrate that the extrapolation given in papers (*4–6*), i.e., the use of the correlation mentioned above, is not sufficiently correct. It will be demonstrated that additional surface reactions also may be involved in the hydrogen consumption during the pretreatment processes.

The first contradiction we found appeared in the preliminary report (*4*). It was mentioned that in the course of HTHT the number of hydrogen atoms consumed was about 10 times as many as that of the total Pt atoms. We believe that this high value cannot be interpreted any other way than to assume additional hydrogen-consuming reactions.

Let us examine data given in the subsequent paper (*5*). In Table 2 (see run No. 2) the value of hydrogen consumed during hydrogen treatment is 1.25 H/Pt (reaction (1a)) and the corresponding oxygen uptake during oxygen treatment calculated from run Nos. 3 and 4 is 0.46 O/Pt (reaction (1b)). The latter value corresponds to 0.92 H/Pt. From this data it follows that in run No. 2 hydrogen corresponding to 0.33 H/Pt (i.e., 1.25 − 0.92) is consumed in an unknown surface reaction (in run No. 5 this value is even greater: 0.49 H/Pt), i.e., either redox reaction (1) should have different stochiometry or additional unknown reactions should be involved in the hydrogen consumption. In this respect there is only one question: what is the reliability of the correlation found if discrepancies of this kind occur in the initial data?

Let us discuss the basic point of the papers mentioned, i.e., the linear correlation found between the H_2 (or O_2) consumption during the pretreatments and the decrease (or increase) in the H/Pt ratio measured by chemisorption (ΔH/Pt) (Fig. 2 in Ref. (*5*) and Fig. 1 in Ref. (*6*)). On both figures the experimental points are very scattered. Although on these two figures the ratio of slopes is close to 2 to 1, the significant scattering of the experimental points raises certain doubts in relation to the reliability of these ratios used as a basic proof for reaction (1). Let us discuss only one point in this respect. In Fig. 2 of Ref. (*5*) it can be seen that the behavior of the catalyst 2% Pt/ALO-4 is quite different than that of the

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catalyst 5% Pt/ALO-2. Upon using the experimental points obtained on the former catalyst the extrapolation applied by Kunimori *et al.* (*5*) resulted in much higher slope ratios than 2 to 1. For this reason it seems to us that it would be more correct to determine the ratio of slopes for each catalyst studied, and to analyze the value of these ratios separately, as it hardly can be rationalized that a generalized linear correlation should exist between the decrease (or increase) in the amount of chemisorption (ΔH/Pt) and the amount of H_2 (and O_2) consumptions during the pretreatment processes for all kinds of supported platinum catalysts with different Pt content and a different type of support. With respect to the Fig. 2 of Ref. (*5*), we have additional questions:

(1) if the aim of this approach was to get a generalized correlation, in this case why were the results obtained on other catalysts (see Table 3 (*5*)) not included in this figure?

(2) can this correlation be extended to catalysts with high initial dispersion values (H/Pt $>$ 1) or to catalysts which showed significant decrease in the H_2 chemisorption (i.e., high ΔH/Pt values) upon applying HTHT (see, e.g., catalyst No. 3, H/Pt = 1.21; catalyst No. 7, H/Pt = 1.04; and catalyst No. 4, H/Pt = 1.25) (*5*)?

(3) in Fig. 2 of Ref. (*5*) the highest value for ΔH/Pt is around 0.75; why were the above-mentioned data with high H/Pt values not used for the correlation?

In light of the contradictions mentioned above we suggest that the hydrogen consumption measured during HTHT can be only partly attributed to a redox-type surface reaction (1); it is more likely that further unknown surface reactions are involved in the hydrogen consumption, and the decrease in the H/Pt ratio upon applying HTHT is a result of a very complex surface phenomena that cannot be attributed exclusively to the redox-type surface reaction (1).

Let us discuss the possible surface reactions responsible for the additional hydrogen consumption. We believe that the sulfur and the chlorine content of the catalysts can be involved in these reactions.

TABLE 1

HTHT Induced Changes in the Cl Content and H/Pt Ratio

Run No.	Pretreatment[a]	Chlorine[b] Residual	Chlorine[b] Lost	H/Pt[c]
1	H_2(300)1.0	1.32	0.01	0.31
2	H_2(500)1.0	1.18 (1.16)[d]	0.18 (0.20)[d]	0.09
3	H_2(630)1.0	0.95	0.24	0.05
4	N_2(500)1.5	1.24	0.11	—
5	O_2(500)1.5	1.25	—	—
6	O_2(400)1.5, H_2(500)1.5	1.03	0.26	0.23
7	O_2(400)1.5, H_2(500)1.5 Two times	0.88	0.54	—

[a] Atmosphere (temperature, °C) time, hours.
[b] Measured as Cl^-; initial Cl content: 1.36 ± 0.06.
[c] By pulse method at 20°C.
[d] After 4 h.

The involvement of the HTHT in the control of the SO_4^{2-} content of the ALO-2 type alumina has been mentioned by Kunimori *et al.* (*5*). The strong correlation between the decrease in the SO_4^{2-} content and the increase of the Pt content may indicate that hydrogen activated by the platinum may play a significant role in the loss of sulfur.

The role of chlorine was entirely omitted in the papers discussed (*4–6*). Reforming Pt/Al_2O_3-type catalysts with a 0.5% Pt load always gives a chlorine content in the range 0.5–1.5%. This means that the atomic ratio of chlorine to Pt is 5–15 to 1. Catalysts with higher Pt content may have even higher chlorine content. In order to demonstrate the role of HTHT in the chlorine balance we carried out the set of experiments shown in Table 1.

Above 300°C formation of HCl was observed in oxygen, nitrogen, and hydrogen atmospheres. In the presence of H_2 the amount of HCl formed was always higher than in its absence. However, consecutive oxygen/hydrogen treatments (run Nos. 6 and 7) resulted in further loss of chlorine. In this case it was suggested that the oxygen treatment was involved in the mobilization of chlorine by formation of $PtCl_xO_y$ (*7, 8*). All of this experimental evidence cannot be interpreted otherwise than to assume hydrogen-involved surface reactions during HTHT.

The catalysts used in the papers discussed (*4–6*) were prepared from H_2PtCl_6 in aqueous solutions and were reduced in hydrogen at 500°C for only 1 h. For these reasons we believe that all of these catalysts should have sufficient chlorine content. As far as the standard pretreatment processes of all catalysts have been carried out under the condition O_2, 450°C; H_2, 300°C (*5*), it can also be suggested that the temperature of the hydrogen treatment is too low to mobilize the surface chlorine. However, upon increasing the temperature of H_2 treatment up to 500°C and varying its duration this process can be more pronounced resulting in higher chlorine loss. In other words it can give higher H_2 consumption values under experimental conditions used in the papers discussed (*4–6*).

All of these data may indicate that the basic approach used in the works discussed, i.e., the use of H_2 or O_2 consumptions (with the corresponding $H/Pt = 2$ and $O/Pt = 1$ ratios), may not be correct as the additional hydrogen-consuming reactions, observed upon applying HTHT, may alter the theoretically expected H/Pt and O/Pt ratios. Consequently, we believe that it was incorrect to use the generalized extrapolation based on the dependence of H_2 (O_2) consumption during the pretreatment procedure vs decrease (or increase) of hydrogen chemisorption (see Fig. 2 (*5*)) as a basic proof for the redox reaction (1). This reaction, as was stated earlier (*1*), may be of importance only at much higher temperatures.

We believe that in the case of supported Pt catalysts the HTHT induces a very complex set of phenomena. One of the key problems in this respect is to get more reliable experimental data, including H/Pt values. However, in order to obtain these data more detailed and confirmed studies are needed.

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