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The State of Platinum in Pt on Sulfated Zirconia Superacid Catalysts

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X-ray photoelectron spectroscopy, X-ray diffraction, and temperature-programmed reduction were used to characterize Pt on both sulfated and nonsulfated zirconia. Upon air calcination of the sulfated sample at 600°C, Pt was reduced to the metallic state. In the case of nonsulfated samples, Pt remained in an oxidized form. It is proposed that SO_2 produced by the decomposition of sulfate ions reduces Pt. © 1994 Academic Press, Inc.

INTRODUCTION

The presence of noble metals in sulfated zirconia superacid catalysts greatly enhances their activity and stability during hydroisomerization reactions (1, 2). Platinum is among the most used metals for this purpose (1–5). The role of platinum during hydroisomerization was given two different interpretations. Based on the assumption that in the presence of platinum, the reaction proceeds via a bifunctional mechanism, Wender and co-workers (1) explained the role of platinum by the enhancement of the hydrogenation function and therefore a better balance between this function and the acid function. On the contrary, Ebitani *et al.* (6, 7) concluded from IR and kinetic studies that (i) the catalyst does not act as a bifunctional catalyst; (ii) the promoting effect of hydrogen is due to the generation of strong protonic acid sites via hydrogen dissociation, followed by spillover and proton formation and finally reaction with an O ion nearby a Lewis acid site; (iii) the electron liberated during the proton formation interacts with the Lewis acid site which then becomes much weaker; and (iv) such weakened Lewis acid sites generate less coke, thus leading to a catalyst with improved stability.

The state of platinum is also a matter of controversy. It has been established that even after reduction, platinum does not show typical metallic properties such as olefin hydrogenation or significant chemisorption of H_2 or CO (6, 8, 9). This behavior could be explained simply by the poisoning effect of sulfur. However, in a recent XPS study. Ebitani *et al.* (8) reported that in the presence of sulfate ions, platinum remains essentially in an oxidized state, even after hydrogen reduction at 400°C. This unexpected behavior prompted us to undertake a detailed characterization study of Pt supported on sulfated zirconia catalysts. The present report is a preliminary account of our findings based on XPS, XRD, and temperature-programmed techniques.

EXPERIMENTAL

Zirconium hydroxide was prepared by hydrolysis of zirconyl chloride (98%, Aldrich) with aqueous ammonium hydroxide (28 wt%, Anachemia) at ambient temperature. The solid was then filtered and thoroughly washed in order to free it of chloride ions, and dried in air at 323 K for 5 days. Sulfation of zirconium hydroxide was carried out by mixing it with a 1 *N* sulfuric acid solution. The amount of acid solution was 10 ml/g of zirconium hydroxide. After 1 h of stirring the solid was filtered and dried again before storage.

Platinum was loaded on both sulfated and nonsulfated zirconia as H_2PtCl_6 using the incipient wetness method. In order to make it easier to extract reliable information from the above-mentioned characterization techniques, a high metal loading (5 wt%) was used. The sulfated sample was calcined in air at 873 K. In order to avoid extensive loss of surface area, the nonsulfated catalyst was often calcined in air at only 673 K. The sulfated and nonsulfated samples will be designated as $Pt/ZrO_2/SO_4^=$ and Pt/ZrO_2, respectively.

XPS spectra were recorded with a V.G. Scientific Escalab Mark II system with an hemispherical analyzer operated in the constant pass energy mode (20 eV). An Mg $K\alpha$ X-ray source ($h\nu = 1253.6$ eV) was used (10). Precalcined samples were loaded in a reactor directly connected to the XPS instrument allowing for *in situ* treatment and analysis without air exposure. Precalcined samples were first reactivated *in situ* under flowing oxygen at 443 K for

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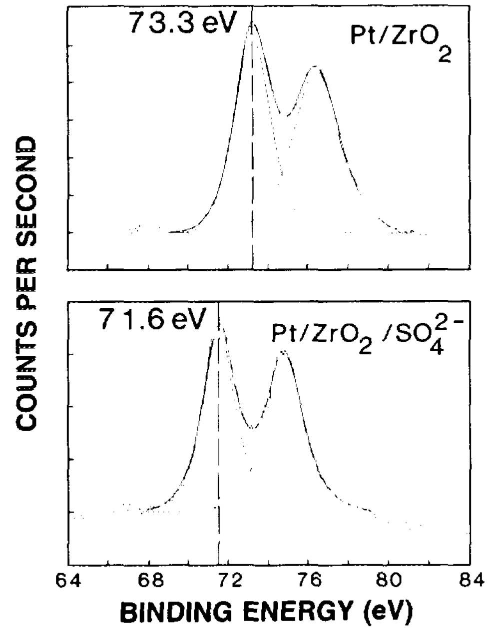

FIG. 1. Pt(4*f*) XPS spectra of samples calcined in air at 600°C (sulfated sample) and 400°C (nonsulfated sample).

2 h before analysis. These are referred to as calcined samples. The same catalysts were submitted to reduction in flowing hydrogen for two hours at 443 and 623 K and analyzed by XPS after each step.

A binding energy of 182.7 eV for the Zr($3d_{5/2}$) level was used as an internal reference for all samples. The binding energy of Zr($3d_{5/2}$) was determined with reference to Au($4f_{7/2}$) = 84.0 eV in duplicate experiments using a gold sputtered sample. These experiments were run separately because of the interference between the Pt(4*f*) and the Au(4*f*) peaks. The position of the Zr(3*d*) after correction for charging effects was found to be independent of the treatment. The alternative of using the C(1*s*) peak of the adventious carbon as a reference was dismissed because this peak was broad and very weak.

XRD spectra were recorded on a Philips PW1010 X-ray diffractometer using a nickel filtered Cu *K*α (λ = 1.506 Å) radiation. Temperature programmed reduction (TPR) experiments were carried out using an Altamira instrument. About 100 to 120 mg of precalcined samples were used. TPR experiments were carried out between room temperature and 1023 K using a mixture of 10.1% H_2 in argon. The heating rate was 10 K/min.

RESULTS AND DISCUSSION

The Pt(4*f*) XPS spectra of Pt on sulfated and nonsulfated zirconia shown in Fig. 1 were recorded immediately after oxygen activation at 443 K. It is seen that the binding energies of Pt($4f_{7/2}$) in Pt/ZrO_2/$SO_4^=$ and Pt/ZrO_2 are 71.6 and 73.3 eV, respectively. Hydrogen reduction of the nonsulfated sample for two hours at 443 K followed by an additional 2 h at 623 K shifted the binding energy of Pt($4f_{7/2}$) first to 72.6 eV, then to 71.7 eV (Fig. 2). Conversely, hydrogen treatment of the sulfated sample at both temperatures had no effect on the binding energy of its Pt($4f_{7/2}$) core level.

For similarly calcined samples, Ebitani *et al.* (8) found Pt($4f_{7/2}$) binding energies of 72.1 and 71.7 eV for nonsulfated and sulfated samples, respectively. Moreover, upon hydrogen reduction at 673 K, the Pt($4f_{7/2}$) binding energy decreased to 71.4 eV for the nonsulfated sample, while it did not change for the sulfated sample. Ebitani *et al.* (8) gave the interpretation that Pt in the sulfated sample is essentially oxidized even under H_2 at 673 K, and that the presence of sulfate ions strongly suppresses the reducibility of platinum.

Our data are at odds with the findings of Ebitani *et al.* (8). On the contrary, our data tend to indicate that in the sulfated sample, platinum is essentially in the metallic state even after calcination at 873 K. Indeed the Pt($4f_{7/2}$) binding energy in this sample was found to be the same as the Pt($4f_{7/2}$) binding energy in the nonsulfated sample

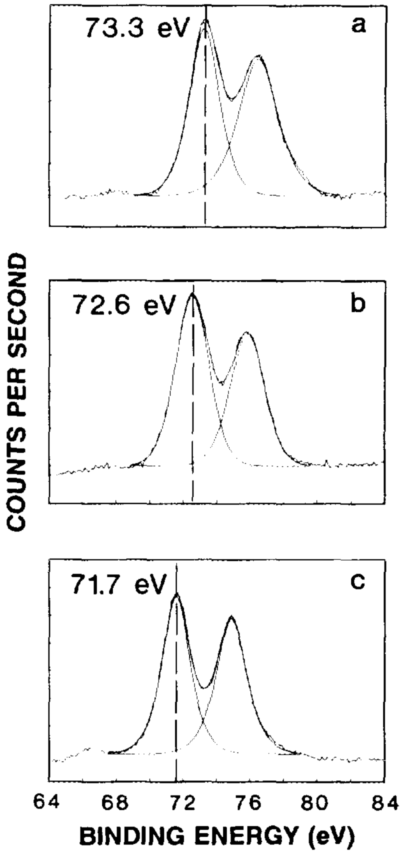

FIG. 2. Pt(4*f*) XPS spectra of nonsulfated samples calcined in air at 400°C (a), followed by hydrogen reduction at 170°C (b) or 350°C (c).

after reduction at 623 K, i.e., 71.7 eV. Lööf *et al.* (11) found that the binding energy of Pt($4f_{7/2}$) in Pt/CeO$_2$ and Pt/Al$_2$O$_3$ reduced in hydrogen at 500°C is 71.6 eV, in full agreement with our own data. In the calcined form, Pt/ZrO$_2$ exhibits a Pt($4f_{7/2}$) binding energy of 73.3 eV, that is 1.6 eV higher than in its sulfated counterpart. This indicates that in calcined, sulfate free catalysts, platinum is actually oxidized.

In order to further support these conclusions, other characterization techniques were used. The XRD pattern of both oxidized samples are depicted in Fig. 3. The sulfated sample shows clearly the main peaks of metallic platinum, i.e., (111) and (200), at 2θ of 39.76 and 46.22°, respectively. The nonsulfated sample exhibits only peaks attributable to ZrO$_2$.

Figure 4 shows some relevant temperature programmed reduction data. As expected, no particular event took place during TPR of pure ZrO$_2$ (Fig. 4a). The TPR profile of nonsulfated Pt/ZrO$_2$ (Fig. 4b) exhibits a single hydrogen consumption peak at 176°C, which is in a reasonable agreement with supported Pt oxide reduction temperature reported in the literature (12). Similar data were obtained with a Pt/ZrO$_2$ sample precalcined at 600°C, except that platinum reduction took place at 122 instead of 176°C. However, it is seen from Fig. 4c that the sulfated Pt/ZrO$_2$/SO$_4^=$ sample does not consume any hydrogen in the relatively low temperature region. This is in agreement with the contention that in this sample, Pt is already reduced and therefore does not consume any hydrogen. The broad peak, the onset of which occurs at about 300°C, with a maximum at 478°C, corresponds to the release of hydrogen sulfide as checked by mass spectrometry (9).

The last TPR profile (Fig. 4d) concerns a Pt-free ZrO$_2$/SO$_4^=$ sample. This profile shows only one strong peak at 671°C corresponding to the formation of SO$_2$ as confirmed by mass spectrometry (9). In the presence of Pt, the gas released during TPR was H$_2$S instead of SO$_2$. Moreover, it was released at a lower temperature than the release of SO$_2$ in the absence of platinum (478 vs 671°C). This suggests that, even though poisoned by sulfur, Pt is capable of dissociating hydrogen at least above 300°C. The availability of atomic hydrogen enhances H$_2$S formation.

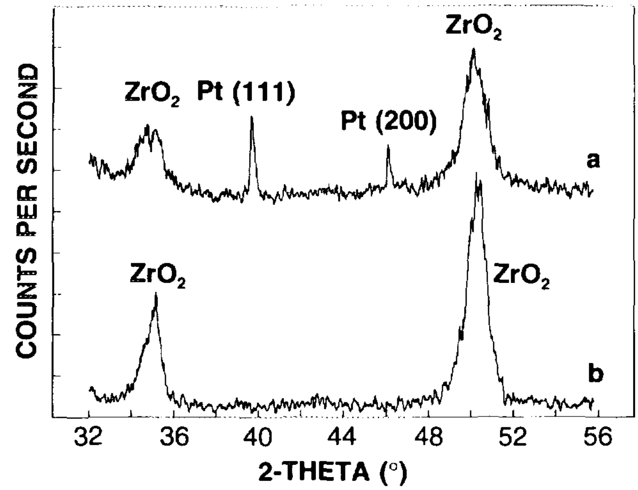

FIG. 3. X-ray diffraction patterns of (a) sulfated and (b) nonsulfated samples calcined in air at 600°C.

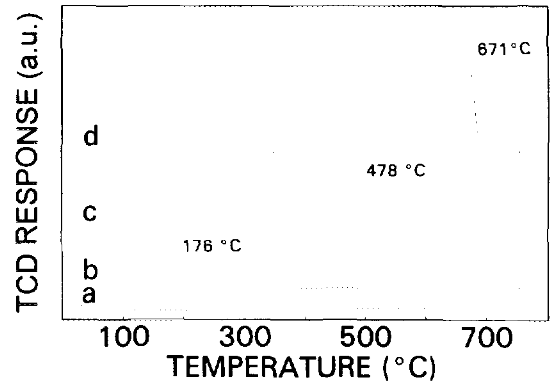

FIG. 4. Temperature-programmed reduction data of samples precalcined in air at the indicated temperatures: (a) ZrO$_2$, 400°C; (b) Pt/ZrO$_2$, 400°C; (c) Pt/ZrO$_2$/SO$_4^=$, 600°C; and (d) ZrO$_2$/SO$_4^=$, 600°C.

Experimental data reported here provide overwhelming evidence for the occurrence of metallic platinum upon air calcination of Pt/ZrO$_2$/SO$_4^=$ at 600°C. The problem as to how metallic platinum is formed under oxidizing conditions at temperatures as high as 600 or even 800°C (9) is not obvious. A reducing species must be generated under air treatment. Moreover the reduction mechanism must involve sulfur containing species since under similar conditions, Pt in nonsulfated Pt/ZrO$_2$ remains oxidized.

Lee and Park (13) found that in flowing helium, sulfate ions in Fe$_2$O$_3$/SO$_4^=$ begin to decompose to produce gaseous SO$_2$ at 480°C. Under flowing 5% O$_2$ in Ar our sulfated samples show broad peaks between 450 and 750°C corresponding to the release of sulfur as SO$_2$ as confirmed by mass spectrometry. Moreover, Lööf *et al.* (11) reported that oxidized platinum can be reduced at 500°C to the metallic state with SO$_2$ even under oxidizing conditions. Therefore, we suggest that during air calcination of Pt/ZrO$_2$/SO$_4^=$, Pt is reduced by SO$_2$ that originates from decomposition of sulfate ions. This behavior seems to be unique to Pt. Preliminary data using Rh, Ru, and Pd indicate that these metals do not undergo the same reduction process as Pt. Further work is underway to uncover the fine details of the proposed reduction scheme.

ACKNOWLEDGMENT

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