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Platinum sulfated zirconia catalysts. Fate of chlorine during activation

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The gases evolved during activation of a sulfated zirconia prepared by impregnation with chloroplatinic acid have been followed using mass spectrometry and infrared spectrometry. When the sample is heated in either helium or in air, the halogen is lost from the catalyst as HCl and Cl_2. Heating the sample in hydrogen results in the loss of the halogen as HCl, and only traces as Cl_2. The loss of halogen occurs over a wide temperature range (200–900°C). The data are consistent with the chloroplatinic acid being converted by loss of halide with the formation of Pt^0.

Keywords: sulfated zirconia, activation of catalyst, platinum, loss of chlorine

1. Introduction

Much of the recent attention devoted to solid sulfated zirconia catalysts has been due to the assertion that they possess superacidity [1,2]. Thus, these catalysts are able to effect reactions that have traditionally been accomplished with liquid sulfuric or hydrofluoric acid. The desire to replace these liquid acids with a more easily contained and far less corrosive catalyst also aroused interest in the sulfated zirconia catalyst. In spite of recent reports questioning the claims of superacidity for the sulfated zirconia, there is no question that the material exhibits superactivity. Thus, the sulfated zirconia catalyst is able to effect the isomerization of *n*-butane at 150°C at rates that attract commercial interest; to accomplish this reaction at similar rates requires at least 100–200°C higher temperature for the most active zeolite catalysts. The interest in the lower temperature operation is due to the thermodynamic equilibrium favoring the desired isobutane isomer at the lower temperatures.

While sulfated zirconia possesses a high initial activity, the catalyst deactivates rapidly unless a hydrogenation function is included in the catalyst formulation. To date either Pt [3,4] or Fe + Mn [5,6] have been used most frequently to provide the hydrogenation (promoter) function. Keogh et al. [7] have shown that the highest catalytic activity for hexadecane conversion occurs with a sulfated catalyst that contains 0.6 to 1.0 wt% Pt.

While most believe that Pt is the preferred metal, there is serious debate over the state of Pt in the working catalyst. Ebitani et al. [8–11] suggest that the unique properties imparted by Pt could be due to the fact that a large fraction of the platinum remains in the form of PtO and PtS with very little of the Pt in the metallic form. Iglesia et al. [10] and Paál et al. [13] present data to show that the Pt is present as small crystals of PtS. Wender et al. [14] suggest that platinum provides the metallic role in a bifunctional mechanism but provide no data to characterize the metallic state of platinum. Sayari and Dicko have reported that calcination in air at high temperature produces metallic Pt [15,16]. XAFS data show that metallic Pt is present in the catalyst after activation in air at 650°C [17]; however, recent XANES/EXAFS data have been interpreted to show that platinum is present as a metallic core overlaid by platinum oxide [18].

It is therefore of interest to follow the fate of the components of the platinum precursor utilized to prepare the catalyst during activation in air. Most catalyst preparation procedures utilize chloroplatinic acid at the source of platinum. To that end, data is reported to identify the temperature range of the evolution of chlorine during activation in air.

2. Experimental

Zirconium oxide was prepared by rapidly precipitating from a 0.3 M aqueous solution prepared from anhydrous $ZrCl_4$ with an excess of NH_4OH to a final pH of 10.5. After washing the precipitate thoroughly with water and then with ethanol to remove most of the bound water, the catalyst was dried in air at 120°C for 2 to 3 days. The chloride content of the final water wash was less than 3 ppm. Sulfation of this powder was accomplished by slurrying the dried material with 0.5 M sulfuric acid (15 ml/g of catalyst). The material was dried

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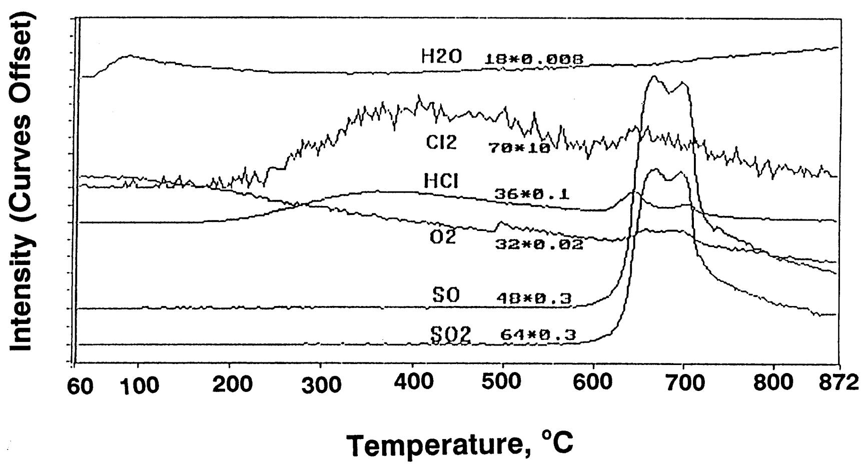

Figure 1. The mass traces for the evolution of gases (during heating a Pt(5 wt%)–SO_4^{2-}–ZrO_2 sample in helium at 20°C/min (numbers represent mass and attenuation, respectively).

overnight at 120°C and then ground to form a powder. The sulfur content of this catalyst was 3.4 wt% after drying and was about 1.0 wt% following calcination at 650°C for 2 h. Appropriate amounts of an aqueous solution of chloroplatinic acid (Colonial Metals, Inc.) were added to the dried powder using the incipient wetness technique. Sufficient platinum was present in the solution to provide a finished catalyst that contained either 1.0 or 5.0 wt% Pt.

Samples were analyzed using a TA TG 2950 instrument that was coupled to a VG mass spectrometer through a flexible fused silica lined flexible capillary tube held at 170°C. It required about 60 ms for gas transfer from the thermal gravimetric analysis/differential thermal analysis (TGA/DTA) system to the mass spectrometer (MS). Each run was conducted using a purge gas (helium, air or hydrogen (5%)/nitrogen mixture) at a total flow of 50 ml/min. A heating rate of 20°C/min was utilized.

In an alternative mode of operation, the DuPont TG 951 instrument could be coupled to a Perkin Elmer 1650 FTIR spectrometer using an insulated Teflon tube held at 150°C. The gas cell (25 × 10 cm) was fitted with KBr windows and was heated to prevent condensation within the cell or the exit tube. Nine FTIR scans could be obtained each 53 seconds and could be stored to be later displayed using either time or temperature scales.

3. Results and discussion

The mass traces obtained during the heating of the 5 wt% Pt sample in helium at 20°C/min from room temperature to 900°C are shown in figure 1. It is observed that water is almost completely eliminated prior to the significant evolution of HCl. Thus, the rate of water evolution attains a maximum at about 150°C and approaches the baseline by the time the temperature has reached about 250°C (figure 2). HCl evolution only becomes measurable at about 200°C and continues to increase to a temperature of about 400°C and then to decline until the temperature has reached 900°C. However, there is another increase in the rate of HCl evolution that appears just ahead of the evolution of the oxides of sulfur (figure 1). The near-coincidence of the evolution of HCl and oxides of sulfur is also illustrated in figure 2. Thus, there appear to be two periods of the evolution of the oxides of sulfur; these have been attributed first to the loss of sulfur from surface species and subsequently to the loss of sulfur from the bulk of the particles [19]. If this is the case, then chloride is apparently eliminated first from surface species and then from bulk species. It should be recalled that the sample was only been dried at 120°C so that there is significant sintering during activation to allow inclusion of both platinum and chloride in the bulk.

Because of the two dominant isotopes of chlorine (^{35}Cl and ^{37}Cl) in the ratio 35 : 37 = 3 : 1, there should be traces corresponding to mass 36 and 38 for the two

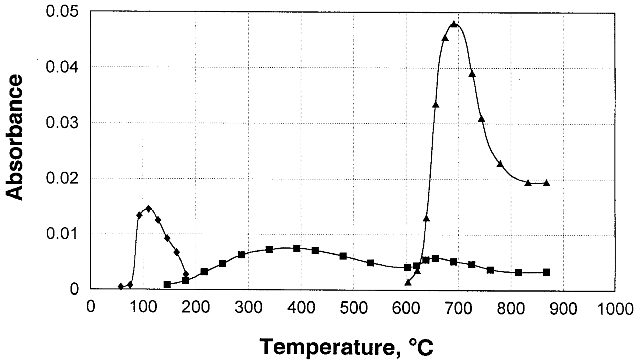

Figure 2. Intensity of FTIR peaks ((■) HCl; (◆) H_2O; (▲) SO_2) during heating a Pt(5 wt%)–SO_4^{2-}/ZrO_2 sample in helium (50 ml/min) at 20°C/min.

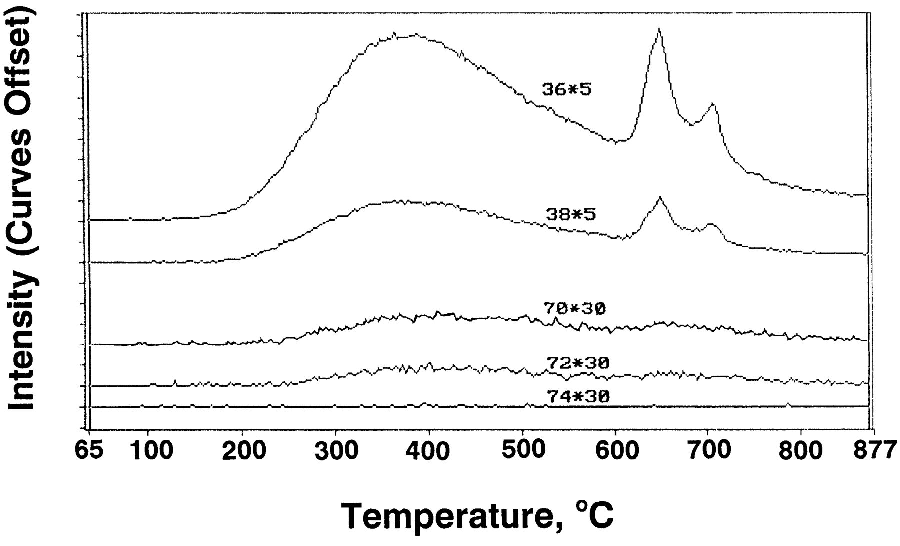

Figure 3. The mass traces for the evolution of the chlorine species (36, $H^{35}Cl$; 38, $H^{37}Cl$; 70, $^{35}Cl_2$; 72, $^{35}Cl^{37}Cl$; and 74 $^{37}Cl_2$) during heating in helium (50 ml/min) at 20°C/min (numbers represent mass and attenuation, respectively).

isotopomers of HCl, and this is observed in figure 3. Furthermore, the ratio of the total areas for these two peaks is in the ratio of the $H^{35}Cl/H^{37}Cl$ is 3 : 1 as expected. In addition to the peaks for the HCl isotopomers, traces corresponding to Cl_2 are also obtained. Furthermore, because of the isotopic abundance one should obtain traces for $^{35}Cl_2 : {}^{35}Cl^{37}Cl : {}^{37}Cl_2$ (mass 70 : 72 : 74) = 100 : 32.4 : 10.5. The area of the trace for the mass 74 peak is insufficient to obtain an accurate area. However, the areas for the mass 72 : 74 peaks occur in a ratio of 100 : 40.6, in reasonable agreement with that expected for the evolution of chlorine.

The 5 wt% Pt sulfated zirconia was also heated at 20°C/min in a flowing air stream. The traces for the evolution of chlorine and sulfur compounds during heating in air are very similar to those obtained when the same sample was heated in helium.

The products from heating the 5 wt% Pt sulfated zirconia in air were also characterized by the use of an infrared instrument coupled by a Teflon tube to the thermal analysis apparatus. A scan of the region of the spectrum between 2500 and 3200 cm^{-1} provided a spectrum containing absorption bands entirely consistent with those expected for HCl. The time (temperature) dependence of the evolution (figure 4) reveals peaks corresponding to HCl being involved in the same temperature region as

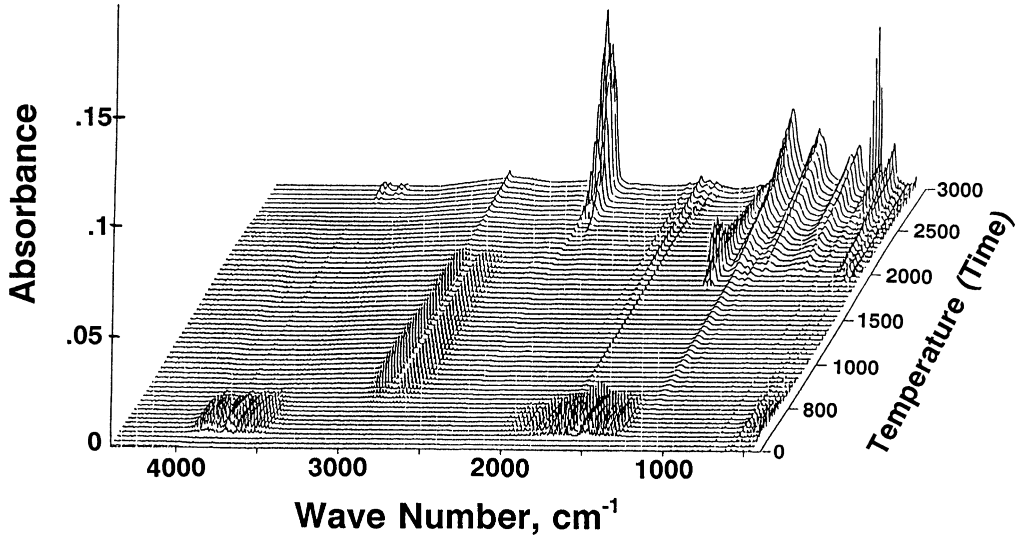

Figure 4. A three-dimensional FTIR plot of the gas species evolved during the heating of Pt (5 wt%)–SO_4^{2-}/ZrO_2 in air (50 ml/min) at 20°C/min.

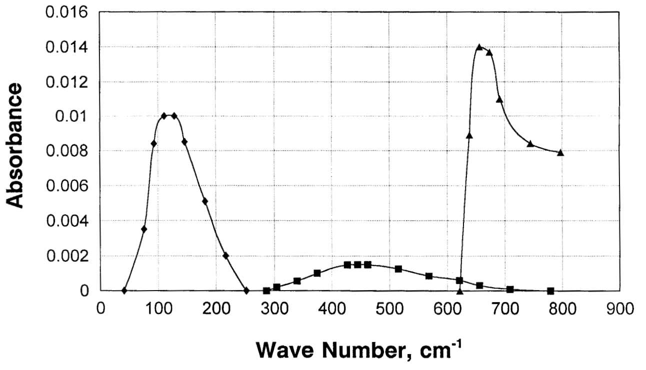

Figure 5. Intensity of FTIR peaks corresponding to HCl (■), H_2O (◆), and SO_2 (▲) during heating of a Pt(1 wt%)–SO_4^{2-}/ZrO_2 sample in air.

was observed for the mass spectrometry data. Thus, two independent types of spectral data have provided data for the identification of the evolution of HCl in the temperature region of 200–900°C.

The traces of the evolution of gases from the 1 wt% Pt sulfated zirconia sample were similar to those of the 5 wt% Pt sample except for the differences in the relative peak areas (figure 5). Thus, the evolution of HCl is observed in the temperature region of 250 to 800°C with a first maximum in the evolution rate at about 450°C and then a second maximum slightly preceding the evolution of the oxides of sulfur.

When the 5 wt% Pt sulfated zirconia sample was heated in a hydrogen and nitrogen mixture (60 ml/min, 10°C/min), HCl was detected in the liberated gases but Cl_2 could not be detected by FTIR; HCl peaks appear in the 2700–3000 cm^{-3} range. Since the HCl peak area, relative to that of sulfur, was much larger when the sample was heated in the hydrogen/nitrogen mixture, it is concluded that the hydrogen reacts with chlorine to produce HCl. It is also evident from the MS data that, unlinke in air of helium, only a trace of Cl_2 was identified when the sample was heated in hydrogen (figure 6). The series of spectra obtained when the 1 wt% Pt sulfated zirconia sample was heated under similar conditions were similar to those except that the HCl peaks were less intense relative to those of the sulfur compounds. As reported previously [20], when the sulfated zirconia sample is heated in hydrogen the sulfur is lost as oxides in a first peak but the sulfur lost in the second peak corresponds to H_2S. Heating a Pt containing sample under similar conditions causes all of the sulfur to be lost as H_2S, indicating that the Pt is present in an active catalytic form that is able to catalyze the reaction between SO_x and H_2 to form H_2S and H_2O.

In an effort to learn whether all of the chloride is lost from the Pt sulfated zirconia sample during activation, a sample was heated to 900°C and held at this temperature until HCl or Cl_2 was not observed in the exit gas. The activated sample was then cooled to room temperature and the inert gas was replaced by a hydrogen/nitrogen mixture. When the sample was again heated to 900°C, no HCl was observed in the exit gas, indicating that all of the chloride had been eliminated during the activation step. Thus, the data indicating that essentially all of the chloride was lost from the sample during activation are in agreement with the chemical analysis of the sample following activation. When heating in helium or air, a significant fraction of the chlorine is eliminated from the surface as HCl and this evolution extends over a wide temperature range. One could envision a reaction such as depicted below as being responsible for the overall process:

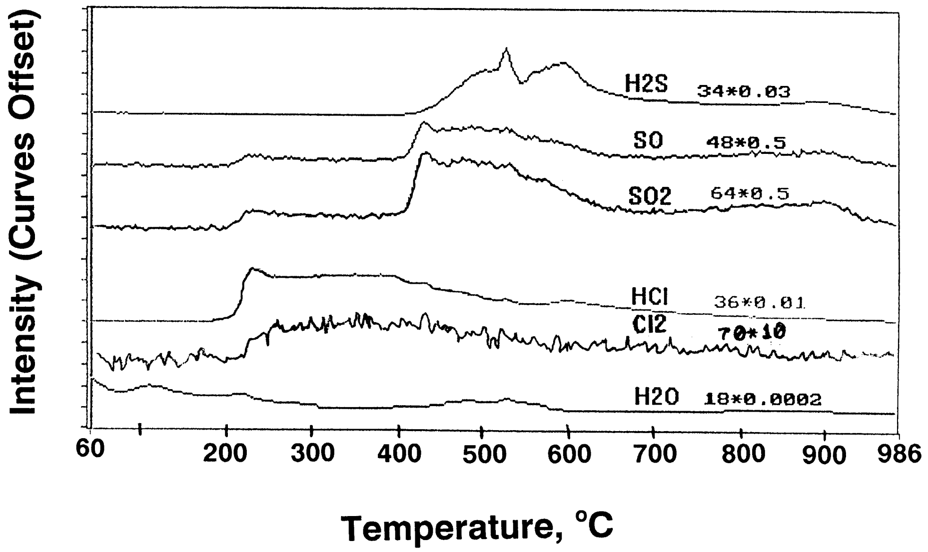

Figure 6. The mass traces for the evolution of gases during heating a Pt(5 wt%)–SO_4^{2-}–ZrO_2 sample in hydrogen at 20°C/min (numbers represent mass and attenuation, respectively).

$$ZrO(OH)_2 \cdot H_2PtCl_6 \rightarrow Pt^0 + 2HCl + H_2O + 2Cl_2 + ZrO_2 \qquad (1)$$

For this reaction the fraction of chlorine eliminated as HCl should be 0.33. Another reaction that could be operating is:

$$[ZrO]^{2+}PtCl_6^{2-} \cdot 2H_2O \rightarrow Pt^0 + \tfrac{1}{2}O_2 + ZrO_2 + 4HCl + Cl_2 \qquad (2)$$

For the latter reaction the fraction of chlorine eliminated as HCl should be 0.67. From the relative areas of the mass traces corresponding to HCl and Cl_2 a value for the fraction of chlorine being eliminated as HCl for the 5 wt% sample is 0.71 and for the 1 wt% sample is 0.75. Thus, the relative areas of HCl and Cl_2 are more consistent with eq. (2) to represent the decomposition of the chloroplatinate ion. We realize that these attempts to represent a complex process by a simple equation provide an idealized situation. However, we have earlier postulated, based upon the amount of water eliminated following the addition of various amounts of sulfate, starting with aqueous sulfuric acid, that a reasonable structure for the sulfate would be $[ZrO][SO_4]$ [14], and this is analogous to the structure shown as the starting material for eq. (2).

In summary, the evolution of chlorine is consistent with the formation of elemental platinum during heating at 650° during two or more hours. If the chlorine is eliminated, as shown by the data presented in this manuscript and by the chemical analyses of activated samples, and platinum does not attain a zero valence state, then some other component, most probably the ZrO_2, must function as the reducing agent. Thus, the loss of chlorine, as observed, would appear to require an oxygen deficient ZrO_2 and an oxygen containing Pt compound, a situation that is considered unlikely considering the relative stability of PtO_2 and ZrO_2.

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