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# XAFS study of the state of platinum in a sulfated zirconia catalyst

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EXAFS and XANES data show that platinum, present in a Pt–$SO_4$–$ZrO_2$ catalyst, exists in the metallic state following calcination in air at 725°C for 2 h, and that no detectable change in the valence state of Pt occurs during use of the catalyst for hydrocarbon conversion at 150°C under hydrogen pressure. The metallic Pt is present in reasonably large crystals where the average coordination number of Pt is about 12.

**Keywords:** Platinum; sulfated zirconia catalysts; XAFS; catalyst characterization; Pt; EXAFS; XANES

## 1. Introduction

The presence of a metal in sulfated zirconia superacid catalysts greatly lengthens the catalyst life [1,2]. Platinum is one of the metals most frequently used for this purpose [3]. A number of rules have been offered for the platinum. Ebitani et al. [4,5] obtained data from their IR and kinetic studies that led them to conclude that the role of platinum is to dissociate hydrogen which spills over and forms a proton. The electron liberated by the formation of a proton interacts with a nearly Lewis acid site; this weaker Lewis site generates less coke, and therefore ages more slowly. Wender and coworkers [1] considered the platinum to function in the Pt–$SO_4$–$ZrO_2$ catalyst as it would in any hydrocracking catalyst by providing a hydrogenation function, presumably as a metal. Keogh et al. [6] reported the platinum in a Pt–$SO_4$–$ZrO_2$ catalyst maintained an ability to hydrogenate 1-octene even after the catalyst had lost its activity toward hydrocarbon or olefin isomerization.

Iglesia [7] advanced the view that platinum was present as a metal sulfide; thus, platinum sulfide provided hydrogenation/dehydrogenation activity as well as providing a site for spillover of hydrogen. Ebitani et al. [8] report that platinum is in an oxidized state even after hydrogen reduction at 350°C. Sayori and Dicko [9] have obtained XPS, XRD and temperature programmed reduction data to support the view that platinum is present in a metallic state following calcination at temperature above about 650–700°C. This is a surprising finding; however, the EXAFS data reported herein support this view.

## 2. Experimental

The zirconia was prepared by precipitation from a zirconyl chloride solution by the rapid addition of an excess of concentrated ammonia (final pH about 10.4) [10]. The precipitate was washed until the water gave a negative test for chloride, then dried at 120°C in air, and impregnated with a 1 N sulfuric acid solution [1,11]. Platinum (1 wt%) was added as a chloroplatinic acid solution by an incipient wetness technique. The $Pt–SO_4–ZrO_2$ sample was calcined in air for 2 h (sample A). A portion of this sample was used for the catalytic studies in a batch reactor for *n*-hexadecane conversion at 150°C under a pressure of about 200 psig of hydrogen for 15 (sample B) or 60 (sample C) min.

X-ray absorption fine structure (XAFS) spectroscopy was taken at beam line IV-3 at the Stanford Synchrotron Radiation Light (SSRL). The radiation was monochromatized with a Si(220) double crystal. The energy band width is 2 eV at the Pt $L_{III}$ edge (11,564 eV). Data were collected with a fluorescent detector with samples at room temperature. The zero energy point (11,564 eV) was defined as the first inflection point in the XAFS spectrum of a thin Pt metal foil. For each measurement typically 2 to 4 energy scans were recorded and summed.

## 3. Results and discussion

The XAFS spectra are subdivided into two spectral regions: the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions. Fig. 1 shows the XANES and the Fourier transform of the EXAFS function, $k^2\chi(k)$. The Fourier transforms for all the samples were taken over a $k$-space range of 3–14 Å$^{-1}$. For Pt metal, the Fourier transform is dominated by a peak at 2.6 Å, corresponding to the nearest Pt coordination shell at 2.774 Å. The shift of the peak position is due to the scattering phase shift $\varphi(k)$. A side lobe at about 2.1 Å, which appears to be a contribution from atoms at another distance, is actually due to complicated features of the phase shift $\varphi(k)$ for heavier elements [12]. The Fourier transform for $PtO_2$ shows a major peak at 1.65 Å, and this is

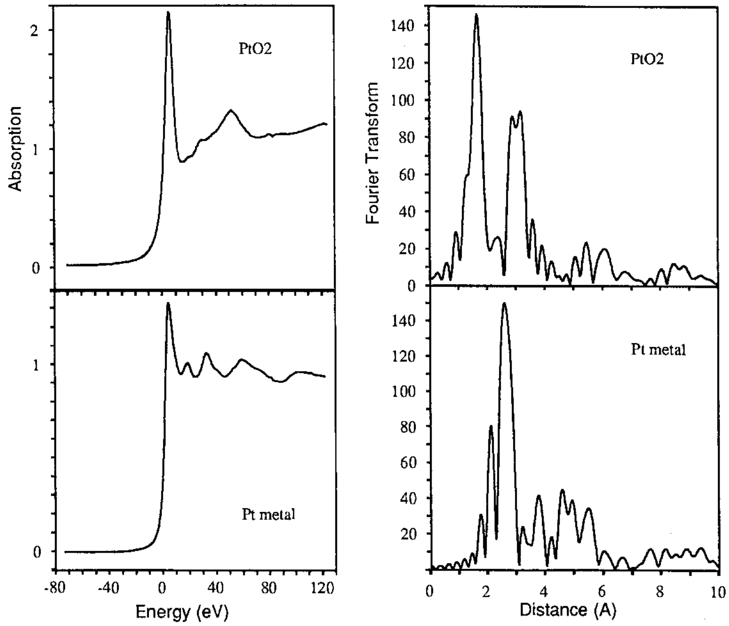

Fig. 1. XANES and EXAFS Fourier transforms for Pt metal foil and $PtO_2$.

assigned to the first oxygen shell at 1.90 Å. The structures in the 2.5–3.5 Å range are contributed by the Pt shells beyond the first oxygen shell.

The XANES and EXAFS Fourier transforms for samples A and B are shown in fig. 2. The spectra for both samples are very similar to the one for the Pt metal foil. To obtain the structural parameters, scattering amplitude and phase shift functions for the Pt–Pt pair were first extracted by fitting the inverse transform of the Pt shell of Pt metal with the known values of coordination number ($N$) and interatomic distance ($R$). These scattering amplitude and phase shift functions were then used as constants to fit the spectra to obtain $N$, $R$ and $\Delta\sigma^2$ for the Pt shell of the three $Pt–SO_4–ZrO_2$ samples. Here $\sigma^2$ is the Debye–Waller factor and $\Delta\sigma^2$ represents the difference between the values of $\sigma^2$ for Pt metal and for the samples. The best fit values are listed in table 1. The differences between the $N$ and $R$ values for the samples and these values for Pt metal are within the uncertainty of the EXAFS analysis ($\Delta N\% = 20\%, \Delta R\% = 1–2\%$); therefore, the data show that the platinum in the $Pt–SO_4–ZrO_2$ samples is completely reduced to the metal. Since there is no significant reduction of $N$ values from that of the Pt foil, the degree of dispersion for the Pt metal phase in the zirconia catalysts is low. The Pt particles should be in the size range of 100 Å, or even larger [13]. EXAFS studies by Via et al. [14] for Pt on $SiO_2$ or $Al_2O_3$ showed that highly dispersed Pt metal clusters were present in these catalysts; this was demonstrated by both the reduction of the Pt peak in the Fourier transform and the coordination number. For Pt on $SiO_2$ or $Al_2O_3$, the Pt shell peak was decreased by 50% compared to that for Pt metal and the fitting gave

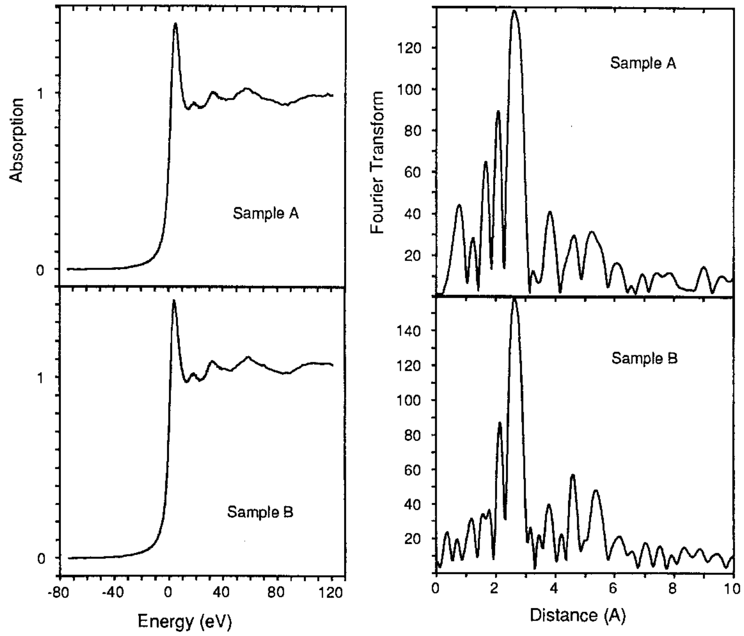

Fig. 2. XANES and EXAFS Fourier transforms for samples A and B.

$N = 7\text{–}8$, with $\Delta\sigma^2 = 0.002\text{–}0.004$. The platinum particles in the sulfated zirconia superacid samples are larger than encountered in typical bifunctional catalysts, such as $Pt\text{–}Al_2O_3$. The presence of Pt in $Pt\text{–}SO_4\text{–}ZrO_2$ in crystals in the 100 Å, or larger, range has been obtained also from our preliminary TEM studies [15].

The XAFS data represent the total platinum in the sample, and therefore the data in figs. 1 and 2 represent both surface and bulk Pt. The coordination numbers ($N_{Pt}$) obtained for the samples are, within experimental error, the same as for the bulk Pt in a Pt foil. Thus, the Pt particles are sufficiently large that is not possible to eliminate the possibility of a monolayer coverage of the Pt particles by chemisorbed $S^{2-}$ and/or $SH^-$. It may be possible to decide whether there is a sulfide monolayer if XAFS data are obtained for a calcined sample before and after adsorbing $H_2S$ on it.

In summary, XAFS studies show that platinum in a $Pt\text{–}SO_4\text{–}ZrO_2$ catalyst is present in the metallic state following calcination at 725°C for 2 h. This result is in agreement with the observation by Sayari and Dicko [9]. One can advance at least

Table 1
Coordination number and interatomic distances comparison for Pt reduced phases

| Sample | $N_{Pt}$ | $R$(Pt–Pt) (Å) | $\Delta\sigma^2$ |
|---|---|---|---|
| sample A | 11 | 2.76 | −0.0009 |
| sample B | 13 | 2.77 | 0.0 |
| sample C | 10 | 2.78 | −0.001 |
| Pt foil (fcc) | 12 | 2.77 | 0 |

two explanations for the formation of metallic platinum during the calcination process. On the one hand, $SO_2$ that is formed directly or from the decomposition of a primary product, $SO_3$, can react with platinum oxide:

$$PtO_2 + 2SO_2 \rightarrow 2SO_3 + Pt\,.$$

This is the reaction preferred by Sayari and Dicko [9]. On the other hand, the oxygen deficiency of zirconium dioxide, when heated to 700°C, may result in the reduction:

$$ZrO_2 \rightarrow ZrO_{2-x} + (x/2)O_2$$

$$ZrO_{2-x} + PtO_2 \rightarrow ZrO_{(2-x)+2} + Pt\,.$$

In either case, metallic Pt is present in the catalyst following calcination at 725°C in air. Use of the calcined $Pt–SO_4–ZrO_2$ catalyst for the conversion of a hydrocarbon at 150°C under a hydrogen pressure does not result in a measurable change in the state of platinum from that of the calcined catalyst.

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