ESR observation of W^{5+} and Zr^{3+} states in $Pt/WO_x/ZrO_2$ catalysts

A. Punnoose and M.S. Seehra

Physics Department, West Virginia University, Morgantown, WV 26506-6315, USA

Received 5 June 2001; accepted 3 October 2001

Electron spin resonance (ESR) studies of $Pt/WO_x/ZrO_2$ catalysts over the temperature range of 5–330 K are reported. Two sets of ESR signals, one with $g_\perp = 1.98$ and $g_\parallel = 1.96$ and the other with $g_x = 1.39$, $g_y = 1.70$ and $g_z = 1.54$ are identified as intrinsic signals from the W^{5+} and Zr^{3+} states, respectively, formed in the sample. These signals are absent in samples without Pt. Studies on samples annealed at 773 K showed possible electron transfer between the W^{5+} and Zr^{3+} states in which the concentration of one state increases at the expense of the other.

KEY WORDS: solid acid catalysts; tungstated zirconia; platinum species; electron spin resonance; W^{5+} and Zr^{3+}

Platinum-promoted tungstated zirconia catalysts ($Pt/WO_x/ZrO_2$) have attracted considerable interest in the recent past due to their high catalytic activity and selectivity for the production of high-octane-index gasoline components [1]. Recent studies by Punnoose *et al.* [2], Barton *et al.* [3,4] and Scheithauer *et al.* [5] have provided considerable insight into the structural and electronic properties of these catalysts. These studies have shown that the tetragonal phase of ZrO_2 acts as the catalyst support [2] and W loading enhances the stabilization of this phase over the monoclinic phase [3–5]. Also the impregnated Pt and WO_x exist as well-dispersed surface species on the tetragonal zirconia support [2–5]. The electronic state of Pt has been in controversy with reports on the presence of both metallic and oxidized forms [1,6–8], and the exact nature of the electronic states of W and Zr is also not well established. Furthermore, the interactions between the different constituents, namely the dispersed Pt and WO_x species and the ZrO_2 support, are far from clear. A proper understanding of these issues is essential for understanding the catalytic mechanism in the $Pt/WO_x/ZrO_2$ (here after PWZ) catalysts.

In this work, we have employed low-temperature electron spin resonance (ESR) spectroscopy, a very powerful tool to study paramagnetic species even in low concentrations, to establish the formation of W^{5+} and Zr^{3+} states in the PWZ catalysts due to oxygen deficiencies in WO_3 and ZrO_2, respectively. The intensities of the ESR signals due to W^{5+} and Zr^{3+} states are affected by thermal treatments and show an inverse correlation strongly suggesting possible electron transfer between the WO_x species and ZrO_2 support. These signals are not observed in WO_x/ZrO_2 (WZ) samples without Pt indicating the possible role of Pt species in the formation of these paramagnetic states. This is the first ever ESR study on the PWZ catalysts. Details of these results follow.

ESR studies reported here were carried out on a standard reflection-type x-band (9.24 GHz) spectrometer employing a Varian cavity and magnet system and a variable temperature cryostat obtained from Oxford Instruments. The measurements were done at different temperatures (5–300 K) on two PWZ samples (PWZ1 and PWZ6) with different loadings of W and a WZ sample without platinum. Both PWZ1 and PWZ6 have 0.5 wt% Pt, but different W loading of 6.5 and 12.5 wt%, respectively. PWZ1 was prepared by co-impregnation of zirconium hydroxide by the solution of tungsten and platinum salts. Zirconium hydroxide was prepared by adding ammonium hydroxide to zirconium chloride. This zirconium hydroxide was modified by co-impregnation of W and Pt using a solution of $(NH_4)_6W_{12}O_{39}{\cdot}xH_2O$ and $H_2PtCl_6{\cdot}6H_2O$ followed by a calcination at 973 K. PWZ6 was prepared in a different way. A zirconium hydroxide sample to which WO_3 (with 12.5 wt% W) had already been added was obtained from Magnesium Elektron, Ltd. (MEL). This tungstated zirconia sample was calcined at 973 K and then was impregnated with Pt followed by another calcination at 773 K. The WZ sample was also a tungstated zirconia (with 12.5 wt% W) sample directly obtained from MEL. These samples were obtained from Professor I. Wender and details of the sample characterization, structural and electronic properties and their catalytic activities have been reported earlier [2,9]. In these experiments, it has been found that pretreating these catalysts at 773 K before loading them into reactors provides better yields of products [9].

ESR spectra of the WZ and PWZ samples recorded at 5 K are shown in figure 1. Two strong signals are observed in the WZ sample at $g = 2.07$ and 4.30 which are marked in the diagram as A and B, respectively. In the PWZ samples, these two signals are also observed with identical ESR parameters in addition to some new signals which will be discussed in detail later. The two signals A and B are not affected by thermal treatments. The presence of paramagnetic oxygen radicals has been reported in WZ catalyst [10] and in numerous other systems [11], but the observed g-values and linewidths of the signals A and B do not match with the ESR parame-

1011-372X/02/0300-0157/0 © 2002 Plenum Publishing Corporation

ters reported for these species. These parameters are also different from those reported for different oxidation states of W and Zr. ESR parameters of the line A are close to those reported for transition metal ions like Cu^{2+} and Fe^{3+}. The g-value of 4.3 observed for line B is reported for Fe^{3+} in different systems in addition to the usual $g \approx 2$ signal [12]. Therefore, we tentatively attribute the two signals A and B observed in the WZ as well as the PWZ samples to a possible paramagnetic impurity, most likely Fe^{3+} present in the sample.

Next we consider the additional lines observed in the PWZ samples. Three sets of new signals could be identified from these additional lines: set I of a group of three lines with g-values 1.70, 1.54 and 1.34 (see figure 1); set II of two lines with $g_\perp = 1.98$ and $g_\parallel = 1.96$ (shown on an expanded scale in figure 2); and set III of a signal at $g \approx 4.3$ which appears as shoulders on the signal B, but with linewidth larger than B (shown in figure 3). In PWZ1, set I is stronger, set II is absent and set III is present as shoulders on the signal B. PWZ6 shows both sets I and II clearly, but set III signal is not clearly visible. This signal might be suppressed in this sample by the overwhelming presence of the impurity signal B. On increasing the temperature to 300 K, the intensity of the signals decreased as expected for paramagnetic species following the Curie law, but no other changes were observed.

In order to interpret the above ESR lines, we first note that stoichiometric WO_3 and ZrO_2 in PWZ with electronic states of W^{6+} ($4f^{14}$) and Zr^{4+} ($3d^{10}$), respectively, should be ESR silent. However, a slight oxygen deficiency in WO_3 and ZrO_2 can lead to the formation of paramagnetic W^{5+} ($5d^1$) and Zr^{3+} ($4d^1$) states and these states have been observed in oxygen deficient WO_{3-x} and ZrO_{2-x} by magnetic susceptibility [13–15] and by electron spin resonance [15–17].

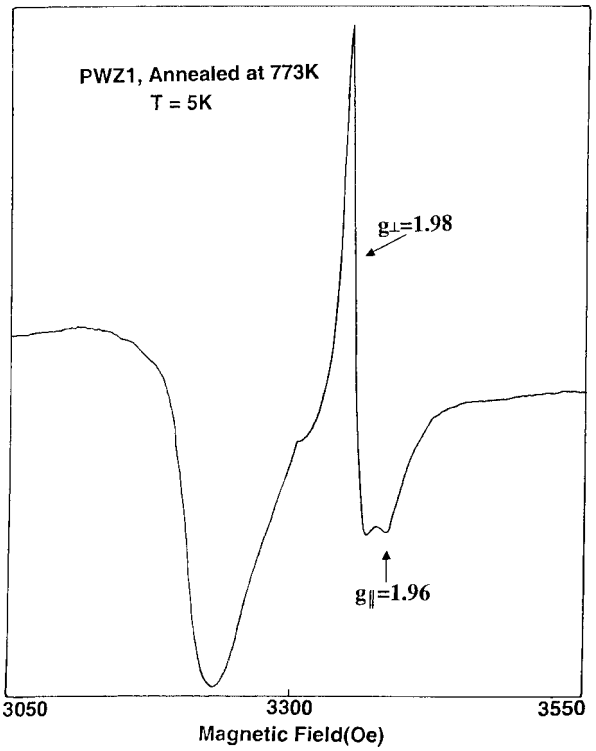

Figure 2. ESR spectrum of PWZ1 (6.5 wt% W, 0.5 wt% Pt) showing the set II signals attributed to Zr^{3+}. The spectrum was recorded at 5 K after annealing the sample in air at 773 K for 3 h.

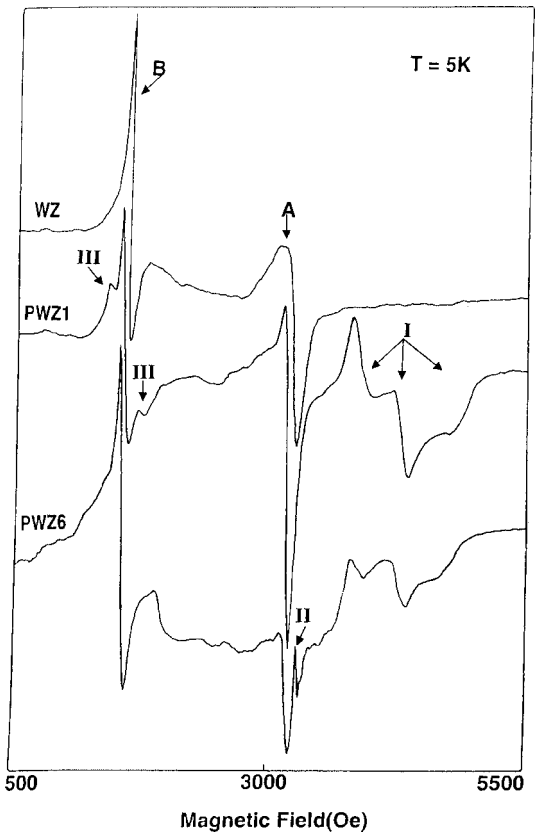

Figure 1. ESR spectra of PWZ1 (6.5 wt% W, 0.5 wt% Pt), WZ (12.5 wt% W, 0 wt% Pt) and PWZ6 (12.5 wt% W, 0.5 wt% Pt) catalysts recorded at 5 K.

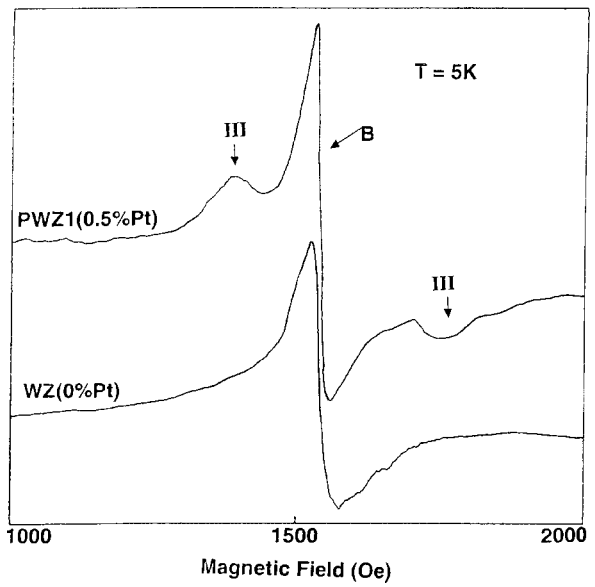

Figure 3. ESR spectrum of PWZ1 (6.5 wt% W, 0.5 wt% Pt) recorded at 5 K showing the set III signal appearing as shoulders on the signal B. The spectrum of the WZ (12.5 wt% W, 0 wt% Pt) sample is also included to illustrate its absence in this sample.

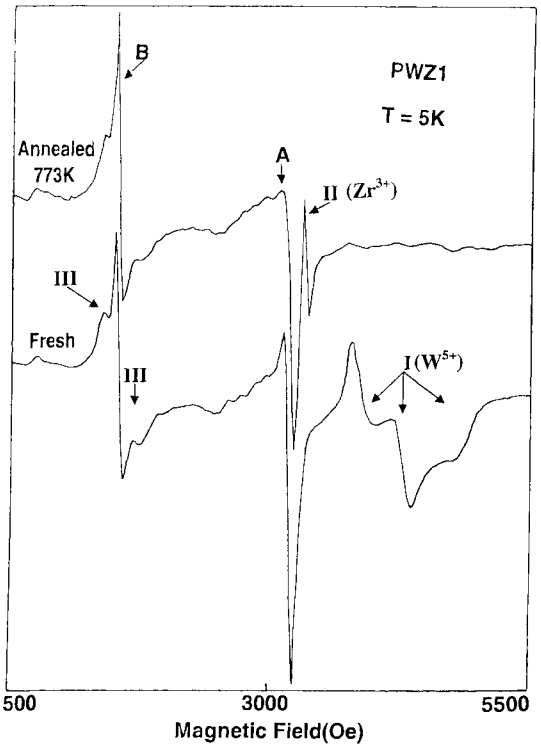

Figure 4. ESR spectra, recorded at 5 K, of fresh PWZ1 (6.5 wt% W, 0.5 wt% Pt) and after annealing it in air at 773 K showing the interplay between the W^{5+} (set I) and Zr^{3+} (set II) signals.

In our recently reported magnetic susceptibility studies on PWZ [2], the observation of a positive susceptibility clearly indicated the presence of paramagnetic species. Both W^{5+} and Zr^{3+} ions being in the d^1 state with tetragonal distortion, the observed g-values for these species are expected to be less than the free spin value of $g = 2.0023$. In our samples, Pt is highly dispersed (71.0% for PWZ1 and 54.5% for PWZ6) [9] so that a partial oxidation of the Pt nanoparticles is quite likely because of their strong affinity for surface passivation [18]. Pt ions oxidized even up to Pt^{4+} (corresponding to the most stable oxide PtO_2) will have more than half filled 5d shell. Any ESR signal from such Pt species will appear in the $g > 2$ region.

On the basis of the above considerations, the sets I and II in the ESR spectra of PWZ samples with $g < 2$ could be originating from W^{5+} or Zr^{3+} states. All features of the signals of set II with g-values $g_\parallel = 1.96$ and $g_\perp = 1.98$ are very close to those reported for Zr^{3+} observed in the ESR spectra of a number of compounds, as illustrated in table 1 [17,19–21]. Therefore, this set of signals are attributed to the Zr^{3+} states formed in our samples. The low g-values of the set I signals ($g_x = 1.39$, $g_y = 1.70$ and $g_z = 1.54$) suggest these signals to be from W^{5+}, which has been observed in several systems (see table 1) with g-values generally in the same range [15,16,22,23]. The g-values, of course, depend greatly on the local symmetry around W^{5+}, which could be different for different compounds resulting in the observed differences. Observation of clear signals of set I with no set II in PWZ1 suggests some oxygen deficiency in WO_3, but ZrO_2 is stoichiometric. PWZ6 has oxygen deficient WO_3 and ZrO_2 to show both set I and set II signals. The g-value of 4.3 of the set III signal which appears as shoulders on the stronger line B is much higher than the average g-values reported for different Pt species such as

Table 1
ESR parameters of W^{5+} and Zr^{3+} observed in different systems

Paramagnetic ion	g-value	Reference
W^{5+} in WO_3	$g_z = 1.532$ $g_x = 1.5054$ $g_y = 1.6612$	Schirmer and Salje [15]
W^{5+} in WO_3/Al_2O_3	$g_\parallel = 1.60$ $g_\perp = 1.722$	Grunert *et al.* [16]
W^{5+} in K_2O–P_2O_5–WO_{3-x} glasses	$1.55 < g_\parallel < 1.65$ $1.65 < g_\perp < 1.75$	Studer *et al.* [22]
W^{5+} in Li_2O-WO_3–P_2O_5 glasses	$1.59 < g_\parallel < 1.6188$ $1.695 < g_\perp < 1.766$	Rakimov *et al.* [23]
W^{5+} in PWZ catalysts	$g_z = 1.54$ $g_x = 1.39$ $g_y = 1.70$	Present work
Zr^{3+} in ZrO_2	$g_\parallel = 1.956$ $g_\perp = 1.981$	Torralvo and Alario [17]
Zr^{3+} in sulfated zirconia	$g_\parallel = 1.967$ $g_\perp = 1.9822$	Vera *et al.* [19]
Zr^{3+} in ZrO_2	$g_\parallel = 1.953$ $g_\perp = 1.978$	Morterra *et al.* [20]
Zr^{3+} in sulfated zirconia	$g_\parallel = 1.951$ $g_\perp = 1.979$	Chen *et al.* [21]
Zr^{3+} in PWZ catalysts	$g_\parallel = 1.96$ $g_\perp = 1.98$	Present work

Pt^{+} and Pt^{3+} [24,25] which are in the range $2.02 < g < 3$. However, recently Scheerer *et al.* [26] have observed a platinum complex in silicon doped with C and Pt giving an ESR signal at $g \approx 4$ with trigonal symmetry. The g-value was explained using a spin Hamiltonian with a large fine structure energy and smaller Zeeman interaction. A possible existence of a similar situation in our samples also with the help of adsorbed oxygen [18] or carbon [27] could be a suitable explanation for the set III signal at $g = 4.3$. The linewidth of our signal is much larger than the one observed by Scheerer *et al.* and so the additional hyperfine structure due to 33.8% ^{195}Pt isotopes (with nuclear spin $I = 1/2$) may not be resolved in our case. Although this is a possibility, this assignment is not firm due to lack of any additional experimental evidence.

The samples were also studied after annealing in air at 773 K for 3 h. This temperature is chosen for annealing since the preparation as well as pretreatment of the PWZ catalysts before loading them into reactors was done at about this temperature [9]. The samples after annealing in air at 773 K for 3 h did not show any structural change in the XRD studies [2]. The WZ catalyst when annealed at 773 K did not show any noticeable change in the ESR spectrum. But when the PWZ samples were annealed at 773 K, clear changes were observed for sets I and II signals. The effect of annealing at 773 K for 3 h on the ESR spectrum of PWZ1 is illustrated in figure 4. After annealing, the set I signals attributed to W^{5+} completely disappeared and strong signals of set II attributed to Zr^{3+}, which were absent in fresh PWZ1, were observed. When different PWZ samples are studied, the intensity of the signals of sets I and II showed an inverse relationship in which the intensity of one set increases at the expense of the other. Aging of the samples also showed similar effects in the intensity of the two sets. This indicates that the ESR active W^{5+} states present in the fresh samples before annealing are converted to ESR silent W^{6+} during the annealing and this process simultaneously triggered the conversion of few ESR silent Zr^{4+} ions to ESR active Zr^{3+}. By annealing PWZ1 at 773 K in air, WO_{3-x} becomes stoichiometric WO_3 by transferring electrons/oxygens from ZrO_2 which makes the latter oxygen deficient ZrO_{2-x}. Thus in the annealed samples, set I signals become absent due to lack of W^{5+} ions and the new strong signals due to the Zr^{3+} states appear. The absence of any ESR signals due to W^{5+} or Zr^{3+} states in the WZ sample in our measurements as well as in an earlier measurement by Yoshinaga *et al.* [10] indicates that in PWZ samples, the passivating nanoparticles of Pt might somehow facilitate the non-stoichiometry in WO_3 and/or ZrO_2. Although the nature of this mechanism is not yet clear, the absence of W^{5+} or Zr^{3+} species in the WZ sample without Pt, even after heat treatment at 773 K, indicates the important role played by Pt in the formation of the W^{5+} or Zr^{3+} species.

Acknowledgment

We thank Professor I. Wender, University of Pittsburgh, for providing the PWZ samples used in this study. This research was supported in part by the US Department of Energy (contract #DE-FC26-99FT40540).

References

[1] M.A. Arribas, F. Marquez and A. Martinez, J. Catal. 190 (2000) 309.
[2] A. Punnoose, M.S. Seehra and I. Wender, Fuel Proc. Technol. (2001), in press.
[3] D.G. Barton, M. Shtein, R.D. Wilson, S.L. Soled and E. Iglesia, J. Phys. Chem. B 103 (1999) 630.
[4] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes and E. Iglesia, J. Catal. 181 (1999) 57.
[5] M. Scheithauer, R.K. Grasselli and H. Knozinger, Langmuir 14 (1998) 3019.
[6] J. Zhao, G.P. Huffman and B.H. Davis, Catal. Lett. 24 (1994) 385.
[7] R.A. Comelli, Catal. Lett. 40 (1996) 67.
[8] T. Shishido, T. Tanaka and H. Hattori, J. Catal. 172 (1997) 24.
[9] S. Zhang, Y. Zhang, J.W. Tierney and I. Wender, Appl. Catal. A 4930 (1999) 1.
[10] Y. Yoshinaga, M. Kudo, S. Hasegawa and T. Okuhara, Appl. Surf. Sci. 121/122 (1997) 339.
[11] J.H. Lunsford, Catal. Mater. (1984) 127, and references therein.
[12] E.M. Yahiaoui, R. Berger, Y. Servant, J. Kliava, L. Cugunov and A. Mednis, J. Phys. Cond. Matter. 6 (1994) 9415, and references therein.
[13] M.J. Sienko and B. Banerjee, J. Am. Chem. Soc. 83 (1961) 4149.
[14] A. Polaczek, M. Pekala and Z. Obuszko, J. Phys. Condens. Matter. 6 (1994) 7909.
[15] O.F. Schirmer and E. Salje, Solid State Commun. 33 (1980) 333.
[16] W. Grunert, W. Morke, R. Feldhaus and K. Anders, J. Catal. 117 (1989) 485.
[17] M.J. Torralvo and M.A. Alario, J. Catal. 86 (1984) 473.
[18] R.W. McCabe, C. Wong and H.S. Woo, J. Catal. 114 (1988) 354.
[19] C.R. Vera, C.L. Pieck, K. Shimizu, C.A. Querini and J.M. Parera, J. Catal. 187 (1999) 39.
[20] C. Morterra, E. Giamello, L. Orio and M. Volante, J. Phys. Chem. 94 (1990) 3111.
[21] F.R. Chen, G. Coudurier, J.R. Joly and J.C. Vedrine, J. Catal. 143 (1993) 616.
[22] F. Studer, N. Rih and B. Raveau, J. Non-Cryst. Solids 107 (1988) 101.
[23] R.R. Rakhimov, D.E. Jones, H.L. Rocha, A.I. Prokofev and A.I. Aleksandrov, J. Phys. Chem. B 104 (2000) 10973.
[24] T. Hulzinga and R. Prins, J. Phys. Chem. 87 (1983) 173.
[25] N.Y. Garces, K.T. Stevens and L.E. Halliburton, J. Appl. Phys. 87 (2000) 8682.
[26] O. Scheerer, M. Hohne, U. Juda and H. Riemann, J. Appl. Phys. 82 (1997) 3456.
[27] L. Maya, E.W. Hagaman, R.K. Williams, X.D. Wang, G.D. Del Cul and J.N. Fiedor, J. Phys. Chem. B 102 (1998) 1951.