## XPS STUDIES OF THE ACIDITY OF WO3/ZrO2 AND NAFION-H CATALYSTS

This study is focusing on the diagnostics of surface acid sites to provide insight into catalyst optimization for coupling alcohols to ethers. The solid acid centers were subjected to quantitative analysis of their concentration and strength by X-ray photoelectron spectroscopy using amines as adsorbing probe molecules. The core-level N 1s photoemission exhibits a large shift towards higher binding energies upon protonation, which occurs upon interaction with Brønsted acid sites. This has been demonstrated with pyridine adsorption on Nafion-H, where the Brønsted acid sites gave rise to a N 1s peak at 401.6 eV compared with physisorbed pyridine at 398.8 eV [13]. Similarly, adsorption of pyridine on sulfated zirconia gave rise to N 1s binding energy peaks at 399.3-399.9 eV and at 401.5 eV, which were attributed to adsorption of pyridine on Lewis and Brønsted acid sites, respectively [13]. Thus, Lewis and Brønsted acid sites can be distinguished and quantified on solid acid catalysts.

For the present studies, the amines chosen were pyridine (a weak base), triethylamine (TEA, a strong base), and ethylenediamine (EDA, a bifunctional base). Survey and high resolution XPS spectral scans of the catalysts were taken before and after amine adsorption. For the zirconia samples, high resolution scans of Zr 3d, C 1s, W 4f, and N 1s regions were carried out. The  $3d_{5/2}$  Zr core-level peak for clean WO<sub>3</sub>/ZrO<sub>2</sub> was chosen as the reference peak for binding energy position.

A survey spectrum of the W/Z catalyst is shown in Figure 12. High resolution scans of the W 4f and Zr 3d peaks were obtained, and the observed binding energies (B.E.) and peak intensities for Zr and W are shown in Table 3 for the "clean" W/Z catalyst prior to adsorption of an amine, where FWHM is the full width at half-maximum of the peak. The peak areas were obtained by first curve-fitting the spectra using a computer program supplied with the Scienta instrument. The spectra were fitted to a Voigt function using at least 10 iterations to obtain a good fit, as defined by a "goodness-of-fit" factor based on the number of data points utilized [13]. The sensitivity factors correspond to the photoelectron cross sections that are based on theoretical calculations by Scofield [16], as tabulated in the Scienta software, but some have been refined in this laboratory by numerous practical measurements [13]. For example, the Scofield cross section for O 1s was given as 2.93, while a sensitivity factor for O 1s of 2.837 was utilized in this work. Similarly, the Scofield cross section given for N 1s was 1.80, while the sensitivity factor used in the present work was 1.62.



FIGURE 12. XPS survey spectrum of the W/Z catalyst.

Peak	B.E. (eV)	FWHM (eV)	Peak Area	Sensitivity Factor	Peak Intensity
Zr 3d <sub>total</sub>			1.598 x 10 <sup>4</sup>	7:04	$2.270 \ge 10^3$
Zr 3d <sub>5/2</sub>	182.19	1.56	9.506 x 10 <sup>3</sup>	4:17	2.280 x 10 <sup>3</sup>
W 4f <sub>total</sub>			$3.722 \ge 10^3$	9.80	3.798 x 10 <sup>2</sup>
W 4f <sub>5/2</sub>	37.57	1.47	1.637 x 10 <sup>3</sup>	4.32	3.789 x 10 <sup>2</sup>
W 4f <sub>7/2</sub>	35.45	1.55	2.079 x 10 <sup>3</sup>	5.48	$3.794 \ge 10^2$

**TABLE 3.** Binding energies and intensities observed for the Zr and W XPS peaks for the clean W/Z catalyst.

After adsorption of pyridine onto the W/Z catalyst using the procedure described in the Experimental section of this report (pp 8-10), the N 1s spectral region was scanned, and the spectrum was resolved into two peaks, as shown in Figure 13. The observed binding energies and peak intensities are given in Table 4. The pyridine adsorption indicated that most of the titrated acid sites were Brønsted acid sites, where the adsorbed pyridine had the N 1s binding energy of 401.64 eV. The presence of a N 1s peak located at lower binding energy was also indicated in the spectrum.

Similar experiments were carried out using ethylenediamine (EDA) as the adsorbing base. The resultant N 1s spectrum is shown in Figure 14. The analysis of the XPS spectral data is compiled in Table 5. It was observed that the two N 1s peaks exhibited similar intensities, indicating the presence of two N species that were approximately equal in number.



FIGURE 13. XPS spectrum of the N 1s peak for the W/Z catalyst after evacuation at 150°C, adsorption of pyridine at ambient temperature, and evacuation at 150°C. The resolved peaks (solid lines) are fitted to the experimental data points.

**TABLE 4.** Binding energies and intensities observed for the Zr and W peaks for the W/Z catalyst after evacuation at 150°C, adsorption of pyridine at ambient temperature, and evacuation at 150°C.

Peak	B.E. (eV)	FWHM (eV)	Peak Àrea	Sensitivity Factor	Peak Intensity
Zr 3d <sub>total</sub>			1.340 x 10 <sup>4</sup>	7.04	1.903 x 10 <sup>3</sup>
Zr 3d <sub>5/2</sub>	182.19	1.38	7.931 x 10 <sup>3</sup>	4.17	$1.902 \ge 10^3$
W 4f <sub>total</sub>	, <del></del>		3.834 x 10 <sup>3</sup>	9.80	3.912 x 10 <sup>2</sup>
W 4f <sub>5/2</sub> /	37.57	1.36	1.691 x 10 <sup>3</sup>	4.32	3.914 x 10 <sup>2</sup>
W 4f <sub>7/2</sub>	35.45	1.47	$2.147 \ge 10^3$	5.48	3.918 x 10 <sup>2</sup>
N 1s <sub>total</sub>			1.425 x 10 <sup>2</sup>	1.62	8.796 x 10 <sup>1</sup>
N 1s <sub>B</sub>	401.64	1.35	9.056 x 10 <sup>1</sup>	1.62	5.590 x 10 <sup>1</sup>
N 1s <sub>L</sub>	400.01	1.35	$3.842 \ge 10^1$	1.62	$2.372 \ge 10^1$



FIGURE 14. XPS spectrum of the N 1s peak for the W/Z catalyst after evacuation at 150°C, adsorption of ethylenediamine at ambient temperature, and evacuation at 150°C.

**TABLE 5.** Binding energies and intensities observed for the Zr and W peaks for the W/Z catalyst after evacuation at 150°C, adsorption of ethylenediamine (EDA) at ambient temperature, and evacuation at 150°C.

Peak	B.E. (eV)	FWHM (eV)	Peak Area	Sensitivity Factor	Peak Intensity
Zr 3d <sub>total</sub>			$1.310 \ge 10^4$	7.04	1.861 x 10 <sup>3</sup>
Zr 3d <sub>5/2</sub>	182.18	1.45	7.765 x 10 <sup>4</sup>	4.17	$1.862 \times 10^3$
W 4f <sub>total</sub>	, <del></del>	•	3.499 x 10 <sup>3</sup>	9.80	$3.570 \ge 10^2$
W 4f <sub>5/2</sub>	37.56	1.38	$1.540 \ge 10^3$	4.32	3.567 x 10 <sup>2</sup>
W 4f <sub>7/2</sub>	35.42	1.47	1.958 x 10 <sup>3</sup>	5.48	$3.573 \ge 10^2$
N 1s <sub>total</sub>		••••••••••••••••••••••••••••••••••••••	4.917 x 10 <sup>2</sup>	1.62	$3.035 \times 10^2$
N 1s <sub>B</sub>	401.57	1.45	$2.022 \ge 10^2$	1.62	1.248 x 10 <sup>2</sup>
N 1s <sub>L</sub>	399.97	1.45	2.286 x 10 <sup>2</sup>	1.62	1.411 x 10 <sup>2</sup>

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Similarly, triethylamine (TEA) was utilized as the absorbing nitrogen-containing base to probe the surface acid sites. The observed N 1s XPS spectrum is shown in Figure 15. Again, the spectrum was adequately fitted by two peaks. The XPS data of TEA on the W/Z catalyst are summarized in Table 6.

The Nafion-H microsaddles (MS) resin catalyst was also characterized by XPS analysis. Nafion-H is a fluorocarbon copolymer containing sulfonyl groups that is an insulating material and suffered charging. Therefore, a hot filament flood gun was utilized to neutralize the charging. In addition, the measured binding energies for Nafion-H samples were adjusted using the C 1s line for poly(tetrafluoroethylene) (PTFE) at 292.48 eV [17] as an internal standard. The F 1s peak for PTFE is observed at 689.67 eV [17].

The data for a clean evacuated Nafion-H MS sample are given in Table 7. Two O 1s binding energy peaks are noted. The higher binding energy peak (535.84 eV) is due to oxygen in ether linkages in the polymer backbone of the resin, while the peak at 533.31 eV corresponds to the oxygen associated with the sulfonic acid groups [10,17]. This is consistent with an O/S ratio = 3 for the sulfonic group, i.e.  $-CF_2SO_3H$ , where the experimental ratio from Table 7 is 2.9.

After evacuation of the Nafion-H MS sample, equilibration with ethylenediamine (EDA) was carried out, and then XPS spectra were obtained after evacuation but without heat treatment of the sample. The resultant N 1s spectrum is shown in Figure 16. The peak could correspond to the amine adsorbed on one uniform Brønsted acid site. However, the peak is slightly asymmetric, and the peak can be fitted by two Gaussians of equal intensity. The N 1s XPS data resolved for two peaks are given in Table 8.



FIGURE 15. XPS spectrum of the N 1s peak for the W/Z catalyst after evacuation at 150°C, adsorption of triethylamine (TEA) at ambient temperature, and evacuation at 150°C.

**TABLE 6.** Binding energies and intensities observed for the Zr and W peaks for the W/Z catalyst after evacuation at 150°C, adsorption of triethylamine (TEA) at ambient temperature, and evacuation at 150°C.

Peak	B.E. (eV)	FWHM (eV)	Peak Area	Sensitivity Factor	Peak Intensity
Zr 3d <sub>total</sub>	,		$1.511 \ge 10^4$	7.04	$2.146 \times 10^3$
Zr 3d <sub>5/2</sub>	182.22	1.31	8.951 x 10 <sup>3</sup>	· 4.17	2.146 x 10 <sup>3</sup>
W 4f <sub>total</sub>	, —		$4.370 \ge 10^3$	9.80	$4.459 \ge 10^2$
W 4f <sub>5/2</sub> /	37.66	1.31	1.930 x 10 <sup>3</sup>	4.32	$4.467 \ge 10^2$
W 4f <sub>7/2</sub>	35.51	1.28	$2.450 \ge 10^3$	5.48	$4.471 \ge 10^2$
N 1s <sub>total</sub>			$2.104 \ge 10^2$	1.62	1.298 x 10 <sup>2</sup>
N 1s <sub>B</sub>	401.74	1.50	$1.527 \ge 10^2$	1.62	9.426 x 10 <sup>1</sup>
N 1s <sub>L</sub>	399.64	1.50	$3.310 \times 10^{1}$	1.62	$2.043 \times 10^{1}$

Peak B.E. Sensitivity FWHM Peak Peak Area (eV) (eV) Intensity Factor F1s 689.72 2.04  $3.811 \times 10^4$  $8.306 \ge 10^3$ 4.5880 S 2p  $9.503 \ge 10^2$  $4.372 \ge 10^2$ 2.1735 ----S 2p<sub>1/2</sub>  $3.166 \ge 10^2$  $4.370 \ge 10^2$ 171.60 1.68 0.7245 S 2p<sub>3/2</sub>  $6.333 \ge 10^2$ 170.27 1.68  $4.371 \ge 10^2$ 1.4490 C 1s<sub>total</sub>  $4.725 \ge 10^3$  $4.725 \ge 10^3$ ---1  $8.826 \ge 10^2$ 1 294.12 1.70  $8.826 \times 10^2$  $3.646 \ge 10^3$ 1  $3.646 \times 10^3$ 292.47 1.45  $1.970 \times 10^3$ 2.50 2.837  $6.944 \ge 10^2$ O 1s 535.84 1.84  $3.609 \ge 10^3$  $1.272 \ge 10^3$ 533.31 2.837

**TABLE 7.** Binding energies and intensities observed for the clean Nafion-HMicroSaddles (MS) catalyst after evacuation.



FIGURE 16. XPS N 1s spectrum of Nafion-H MS after adsorption of ethylenediamine (EDA), with no thermal post-treatment.

Peak	B.E. (eV)	FWHM (eV)	Peak Area	Sensitivity Factor	Peak Intensity
F 1s	689.76	2.06	$4.224 \ge 10^4$	4.5880	9.206 x 10 <sup>3</sup>
S 2p			3.379 x 10 <sup>2</sup>	2.1735	$1.555 \ge 10^2$
S 2p <sub>1/2</sub>	171.46	2.64	$1.120 \ge 10^2$	0.7245	1.546 x 10 <sup>2</sup>
S 2p <sub>3/2</sub>	170.09	2.36	$2.240 \times 10^2$	1.4490	1.546 x 10 <sup>2</sup>
C 1s <sub>total</sub>			5.347 x 10 <sup>3</sup>	1	5.347 x 10 <sup>3</sup>
	294.09	1.82	$1.360 \ge 10^3$	l	1.360 x 10 <sup>3</sup>
	292.47	1.44	$3.832 \times 10^3$	1	$3.832 \times 10^3$
O 1s	536.27	2.21	$1.904 \ge 10^3$	2.837	$6.711 \ge 10^{2}$
	533.21	2.08	1.966 x 10 <sup>3</sup>	2.837	$6.930 \ge 10^2$
N 1s <sub>total</sub>			$1.317 \ge 10^3$	1.62	8.130 x 10 <sup>2</sup>
	402.55	2.51	6.584 x 10 <sup>2</sup>	1.62	$4.064 \ge 10^2$
-	401.03	· 2.16	$6.584 \ge 10^2$	1.62	$4.064 \ge 10^2$

**TABLE 8.** Binding energies and intensities observed for the Nafion-H MS catalyst after adsorption of ethylenediamine (EDA), with no thermal post-treatment.

The Nafion-H MS sample with the adsorbed ethylenediamine (EDA) was subsequently evaculated while being heated at 150°C. The sample was then analyzed again by XPS at ambient temperature, and the resultant N 1s spectrum is shown in Figure 17. The top of the peak appears to be flatter, and the peak can again be resolved into two peaks of equal intensity. The analysis of the XPS data is tabulated in Table 9.



FIGURE 17. XPS N 1s spectrum of Nafion-H MS after adsorption of ethylenediamine (EDA), followed by a thermal post-treatment at 150°C.

As shown, the titration of acid sites gives different results with the different amines. Pyridine titrates 13% of the Brønsted acid sites, while TEA, a strong base that could be sterically hindered on the surface, titrates 22% of the acid sites. EDA titrates 37% of the Brønsted acid sites. Therefore, the accessibility of the Brønsted acid sites on W/Z follows the order of EDA > TEA > pyridine, while the basicity of the amines follows the order TEA > EDA > pyridine. The tungstated zirconia ia not the same as the sulfated zirconia (S/Z). With the latter catalyst, pyridine titrates all Brønsted acid sites, while that is not the case with the tungstated zirconia.

**TABLE 9.** Binding energies and intensities observed for the Nafion-H MS catalyst after adsorption of ethylenediamine (EDA), followed by thermal post-treatment of evacuation at 150°C.

Peak	B.E. (eV)	FWHM (eV)	Peak Area	Sensitivity Factor	Peak Intensity
F 1s	689.74	2.16	$4.265 \ge 10^4$	4.5880	9.296 x 10 <sup>3</sup>
S 2p	~~-		2.709 x 10 <sup>2</sup>	2.1735	1.206 x 10 <sup>2</sup>
S 2p <sub>1/2</sub>	171.75	2.64	9.046 x 10 <sup>1</sup>	0.7245	1.249 x 10 <sup>2</sup>
S 2p <sub>3/2</sub>	170.26	2.36	1.809 x 10 <sup>2</sup>	1.4490	$1.248 \times 10^2$
C 1s <sub>total</sub>			5.581 x 10 <sup>3</sup>	l	5.581 x 10 <sup>3</sup>
	294.09	1.82	1.716 x 10 <sup>3</sup>	1	1.716 x 10 <sup>3</sup>
	· 292 <b>.</b> 47	1.44	3.693 x 10 <sup>3</sup>	1	3.693 x 10 <sup>3</sup>
O 1s	536.22	2.21	$2.008 \ge 10^3$	2.837	$7.078 \times 10^2$
	533.26	2.08	1.496 x 10 <sup>3</sup>	2.837	5.273 x 10 <sup>2</sup>
N 1s <sub>total</sub>			$9.404 \ge 10^2$	1.62	$5.805 \times 10^2$
:	402.71	2.51	$4.701 \ge 10^2$	1.62	$2.902 \times 10^2$
	401.26	2.16	$4.701 \ge 10^2$	1.62	$2.902 \times 10^2$

It is concluded from this study that the amine bases titrate the Bronsted acid sites on these acid catalysts. However, the surface concentration of the accessible acid sites on the tungstena/zirconia catalyst is lower than expected from the tungstate content and are more diluted than observed with the Nafion-H catalyst. In addition, the Bronsted acid sites on the tungstena/zirconia catalyst are heterogeneous since stronger amine bases detect more acid sites.