OPTICAL PROPORTIES OF THE CATALYSTS

Diffuse reflectance studies were carried out in the ultraviolet/visible/near-infrared (UV/Vis/NIR) spectral regions to provide information on the electronic structure, the degree of hydration, and presence of hydroxyl groups of zirconia, tungstena/zirconia, and sulfated _ zirconia samples.

Spectral Data and Analysis. The optical spectra of the three dehydrated samples were collected over the range of 4,500-50,000 cm⁻¹. The diffuse reflectance spectra (DRS) over this full spectral range are shown in Figure 9. It is clear that the optical properties of the three samples reflect the structure and composition of the catalysts.



Figure 9. The diffuse reflectance spectra of monoclinic zirconia (m-ZrO₂), tetragonal SO₄-impregnated zirconia (SO₄/t-ZrO₂), and tetragonal WO₃-impregnated zirconia (WO₃/t-ZrO₂) between 4,500 and 50,000 cm⁻¹.

The spectra in the NIR region are shown in Figure 10. For the three samples, the two particular bands of interest in the NIR region are the H₂O ($\nu + \delta$) band at about 5,250 cm⁻¹, which is a combination of stretching and bending modes, and the mixed H₂O (2ν) + OH (2ν) overtone band of the OH stretch at approximately 7,200 cm⁻¹. The former can be used to monitor the degree of dehydration, while the latter can be used to monitor the hydroxyl groups, which are Brønsted acid sites. These groups are present on ZrO₂. Upon sulfating the zirconia, a larger peak at 7159 cm⁻¹ was observed, corresponding to an increased number of hydroxyl groups (Brønsted acid sites). Upon tungstating the zirconia, a high optical background was observed and the number of free hydroxyls detected greatly decreased, as indicated by the low intensity of the 7092 cm⁻¹ band compared with the ZrO₂ bands.



Figure 10. DRS in the NIR region of monoclinic zirconia, tetragonal SO₄-impregnated zirconia, and tetragonal WO₃-impregnated zirconia in the spectral range of 4,500 and 8,000 cm⁻¹. Peak positions are labelled, but accurate calibration needs to be carried out.

The difference spectrum in the OH NIR region of the WO₃/ZrO₂ catalyst was derived for comparison with the distinct spectrum of ZrO₂ that exhibits two peaks. The absorption spectrum for WO₃/ZrO₂ is shown on the same scale as for ZrO₂ in Figure 11. Also shown is the difference spectrum for WO₃/ZrO₂ that was obtained by magnifying the Kubelka-. Munk transformed spectra by a factor of 10 and subtracting the background. The diminished intensity of the OH frequencies upon surface impregnation of the zirconia with tungstate indicates bonding of the tungstate species to the surface of the zirconia via the surface hydroxyl groups and that it is spread on the surface. There are relatively few hydroxyls present on the tungstated zirconia surface, and those exhibit a shift from \approx 7205 cm⁻¹ on monoclinic zirconia to *ca*. 7120 cm⁻¹ on the tungstated zirconia surface, perhaps arising from low-concentration Brønsted acid sites on the tungstate overlayer.



FIGURE 11. The NIR-DRS spectra of the hydroxyl absorption region for monoclinic zirconia and tetragonal tungstated zirconia on the same relative scale, along with the magnified difference spectrum obtained for the latter sample.

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The areas of the two bands in the NIR region at about 5,250 cm⁻¹ [H₂O ($\nu + \delta$) combination band] and at approximately 7,200 cm⁻¹ [mixed H₂O (2ν) + OH (2ν) overtone band] were calculated for each sample by subtracting a linear background and fitting multiple (usually 3-5) Gaussians to the bands. The areas of the Gaussians in the peak were then summed, and the results of the Gaussian fitting are shown in Table 1.

The approximate concentrations of hydroxyls on the three samples were then calculated based on the assumption that the relative intensities of the H₂O ($\nu + \delta$) and H₂O (2ν) bands were in the ratio of 5/1, as in earlier studies [15]. The equation, derived from this work, to calculate the intensity of the OH (2ν) band from the intensities of the mixed H₂O (2ν) + OH (2ν) overtone band and the H₂O ($\nu + \delta$) combination band is

 $\mathbf{I}_{[\text{H2O}(2\nu) + \text{OH}(2\nu) \text{ mixed band}]} = \mathbf{I}_{\text{OH}(2\nu)} + [\mathbf{I}_{\text{H2O}(\nu+\delta)} / 5], \quad (6)$ where \mathbf{I} = the integrated intensity or peak area.

The hydroxyl concentration of the tetragonal zirconia impregnated with surface sulfate was determined in this laboratory [13] using a method of controlled incremental adsorption and desorption of different nitrogen-containing bases. The surface sulfate concentration was found to be 0.55 monolayer. The concentrations of hydroxyls on the tetragonal WO₃-impregnated zirconia and on monoclinic zirconia were calculated by using the known hydroxyl concentration of the tetragonal SO₄-impregnated zirconia, calculated as I _{OH(2v)} intensities, and Equation 6 given above. The calculated hydroxyl concentrations are given in Table 2. In all cases, the OH surface concentration was determined to be appreciably less than one monolayer.

Table 1. The Gaussian fitting results of the $H_2O(v + \delta)$ combination bands and the mixed $H_2O(2v) + OH(2v)$ overtone bands in the NIR regions of monoclinic zirconia, tetragonal SO_4 -impregnated zirconia, and tetragonal WO₃-impregnated zirconia as determined by DRS.

Sample	2ν Bands (H ₂ O and OH)			$H_2O(v + \delta)$ Bands		
m- ZrO ₂	No. of Gaussian Peaks In Band			No. of Gaussian Peaks In Band		
	Peak	Peak Center	Peak · Area	Peak	Peak Center	Peak Area
	1	7424.095	0.0473	1	5364.610	0.0304
	2	7144.920	0.6076	2	5301.622	0.0278
	3	7348.438	0.1703	3	5228.950	0.1210 .
	4	7208.340	0.6081	4	5158.892	0.0193
			· · ·	5	5129.900	0.2517
	Total Peak Area: 1.4332			Total Peak Area: 0.4502		
<u>}-</u>	No. of Gaussian Peaks In Band					
₩	No.	of Gaussian F In Band	eaks	No. (of Gaussian P In Band	eaks
94 _ 1 -	No. (Peak	of Gaussian F In Band Peak Center	Peaks Peak Area	No. o Peak	of Gaussian F In Band Peak Center	eaks Peak Area
-	No. (Peak 1	of Gaussian F In Band Peak Center 7612.789	Peaks Peak Area 0.2289	No. o Peak 1	of Gaussian F In Band Peak Center 5077.164	Peaks Peak Area 0.1458
• WO ₃ /	No. (Peak 2	of Gaussian F In Band Peak Center 7612.789 7508.370	Peaks Peak Area 0.2289 0.0415	No. 6 Peak 1 2	of Gaussian F In Band Peak Center 5077.164 5155.256	Peaks Peak Area 0.1458 0.4088
WO ₃ / t-ZrO ₂	No. 6	of Gaussian F In Band Peak Center 7612.789 7508.370 7369.754	Peaks Peak Area 0.2289 0.0415 0.0699	No. 6 Peak 1 2 3	of Gaussian P In Band Peak Center 5077.164 5155.256 5244.010	Peaks Peak Area 0.1458 0.4088 0.4266
WO ₃ / t-ZrO ₂	No. 6	of Gaussian F In Band Peak Center 7612.789 7508.370 7369.754 7124.459	Peaks Peak Area 0.2289 0.0415 0.0699 0.3093	No. 6 Peak 1 2 3 	of Gaussian F In Band Peak Center 5077.164 5155.256 5244.010	Peaks Peak Area 0.1458 0.4088 0.4266
WO ₃ / t-ZrO ₂	No. 6	of Gaussian F In Band Peak Center 7612.789 7508.370 7369.754 7124.459 6987.467	Peaks Peak Area 0.2289 0.0415 0.0699 0.3093 0.1835	No. o Peak 1 2 3 	of Gaussian F In Band Peak Center 5077.164 5155.256 5244.010	Peaks Peak Area 0.1458 0.4088 0.4266
WO ₃ / t-ZrO ₂	No. 6	of Gaussian F In Band Peak Center 7612.789 7508.370 7369.754 7124.459 6987.467 6842.649	Peaks Peak Area 0.2289 0.0415 0.0699 0.3093 0.1835 0.1093	No. o Peak 1 2 3 	of Gaussian P In Band Peak Center 5077.164 5155.256 5244.010	Peaks Peak Area 0.1458 0.4088 0.4266

Sample	2ν Bands (H ₂ O and OH)			$H_2O(v + \delta)$ Bands		
SO ₄ / t-ZrO ₂	No. of Gaussian Peaks In Band			No. of Gaussian Peaks In Band		
	Peak	Peak Center	Peak Area	Peak	Peak Center	Peak Area
	1	7147.057	0.5412	1	5354.494	0.0060
	2	7116.763	1.9706	2	5264.007	0.4595
				3	5197.272	0.0426
				4	5181.609	0.7589
	Total Peak Area: 2.5118			Total Peak Area: 1.2670		

TABLE 2. The hydroxyl concentrations calculated from the diffuse reflectance spectra, given in monolayers, of monoclinic zirconia, tetragonal WO_3 -impregnated zirconia, and tetragonal SO_4 -impregnated zirconia.

Sample	I _{OH (2v)}	OH Conc. (monolayers)
ZrO ₂	0.74607	0.18
WO ₃ /ZrO ₂	1.34345	0.33
- SO ₄ /ZrO ₂	2.25835	0.55

Conclusions from Optical Spectroscopy. The samples have well-developed band edges, especially for the monoclinic ZrO_2 with a band edge at about 42,000 cm⁻¹. For the tetragonal SO_4/ZrO_2 catalyst, the band edge is shifted to the UV region (\approx 45,000 cm⁻¹), while for the tetragonal WO₃/ZrO₂ catalyst, the band edge is shifted toward the visible (VIS) region (\approx 35,000 cm⁻¹) and has a very large intensity with an extended tailing. The spectra can be used for diagnostics/quality control of preparation, in combination with XRD. The NIR peaks in the 5,000-5,500 cm⁻¹ region confirm the presence of water in these samples. Assignment of the NIR bands is difficult when a sample is not fully dehydrated, but the spectral shoulders below the peaks at 7159 and 7202 cm⁻¹ in the tetragonal SO_4/ZrO_2 and monoclinic ZrO_2 , respectively, are indicative of weakly bonded hydroxyls. A very slight shoulder is barely detectable on the peak at 7092 cm⁻¹ in the tetragonal WO_3/ZrO_2 spectrum, suggesting that this sample was only partially hydroxylated.

The NIR spectra give information about sample hydroxylation. It is shown that ZrO_2 has a low degree of hydroxylation ($\approx 18\%$) and has little water of hydration associated with it. The hydroxyl concentration of the tetragonal SO_4/ZrO_2 catalyst was determined early [13] and can be used as a "benchmark", The tetragonal WO_3/ZrO_2 catalyst has weak and broad features in the hydroxyl region of the spectrum and is difficult to analysze. However, it is clear that this catalyst is less hydroxylated than the SO_4/ZrO_2 catalyst. It is noted that the WO_3/ZrO_2 catalyst has a larger electronic background in the NIR region than the other two catalysts. Quantitative analysis of the hydroxyl species in these catalysts has been carried out, but more calibration studies with reference systems are needed to achieve greater accuracy.

The UV regions of the spectra reflect electronic band-to-band transitions and show significant differences among the samples. Strong bands in the 35,000 to 48,000 cm⁻¹ spectral range are observed. The spectral inflection point of tetragonal SO_4/ZrO_2 occurs at 45,000 cm⁻¹. The inflection points of the band edges of monoclinic ZrO_2 and tetragonal WO_3/ZrO_2 samples occur at about 42,225 and 34,300 cm⁻¹, respectively. In addition, the tetragonal WO_3/ZrO_2 sample shows a weak band near 25,000 cm⁻¹, while the monoclinic

ZrO_2 shows a very weak band near 32,500 cm⁻¹. These transitions giving rise to these bands

can be intrepreted theoretically based on electronic structure.