Structural Determination of Bulk and Surface Tungsten Oxides with UV–vis Diffuse Reflectance Spectroscopy and Raman Spectroscopy

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Combined UV–vis diffuse reflectance spectroscopy (DRS) and Raman spectroscopy were applied to examine the electronic and molecular structures, respectively, of well-defined W(VI) bulk mixed oxide reference compounds consisting of (i) isolated WO₅ or WO₆ monomers, (ii) dimeric O=W−O=W₃, (iii) polymeric chain of alternating WO₅/WO₆ units, and (iv) WO₆-coordinated W₉=W₁₈ clusters. Raman spectroscopy was employed to confirm the identity and phase purity of the different tungsten oxide structures. UV–vis DRS provided the corresponding electronic edge energy (E₉) of the ligand-to-metal charge transfer (LMCT) transitions of the W(VI) cations. A correlation between the edge energy and the number of covalent bridging W=O−W bonds around the central W(VI) cation was found with E₉ linearly decreasing with increasing number of bridging W=O−W bonds. However, a direct relationship between E₉ and the domain size, N_W, for finite WO₆ clusters does not exist. Subsequently, UV–vis and Raman spectroscopy information were applied to determine the local structures of the molecularly dispersed surface W(VI) species present in supported WO₃/Al₂O₃, WO₃/ZrO₂, and WO₃/SiO₂ catalysts under ambient and dehydrated conditions.

1. Introduction

Supported tungsten oxide catalytic materials are extensively used as heterogeneous catalysts for numerous petroleum, chemical, and environmental processes:¹–³ C₄−C₈ alkane isomerization (WO₃/ZrO₂),⁴–¹⁰ hydrodesulfurization (HDS),¹¹ hydrocarbon cracking (WO₃/Al₂O₃),¹²–¹⁵ olefin metathesis (WO₃/SiO₂),¹⁶–¹⁹ and selective catalytic reduction of NOₓ (WO₃/TiO₂).²⁰–²³ Supported tungsten oxide catalysts have been extensively characterized in the literature with various spectroscopic techniques that provide molecular and electronic structural details as well as surface chemical characteristics.⁶,¹⁰,²⁴–³²,⁹⁰ The molecular and electronic structures of the surface WO₆ species present in supported WO₃ catalysts, however, are still not completely resolved. Knowledge of the local structure of the surface tungsten oxide species plays an important role in the synthesis and optimization of supported tungsten oxide catalyst systems for targeted applications.

UV–vis diffuse reflectance spectroscopy (DRS) has increasingly been employed to investigate the local structure of W(VI) oxide compounds/mixed oxides,³³–³⁴ W(VI) mesoporous materials,³⁵–³⁶ W(VI) polyoxometalates,³⁷–³⁹ and supported W(VI) catalysts.⁵,¹⁰,³⁵,⁴⁰–⁴⁷ In these investigations, the local structures of the W(VI) cation is often associated with the bond positions of the ligand-to-metal charge transfer (LMCT) transitions in the ultraviolet, visible, and near-infrared regions. An important advantage of the UV–vis spectroscopic technique is its ability to function under ambient, dehydrated, and reaction conditions.⁴⁸–⁴⁹

Although the UV–vis DRS LMCT transitions tend to be quite broad, recent publications have indicated that the edge energy (E₉) of the LMCT transition can be quantified and contain information about the local structures of bulk and surface V(V) and Mo(VI) metal oxides.⁵⁰–⁵² Early studies by Weber⁵² analyzed the UV–vis DRS edge energies of bulk molybdenum oxide samples from a number of different publications and found a correlation between the edge energy and the number of next nearest metal neighbors (N_M) of the Mo oxide compounds (Mo=O−Mo bonds), where M represents the degree of aggregation of the MoOₓ structure. Analogous UV–vis DRS E₉−structure relationships have successfully been developed by Gao et al.⁵⁰ for oxides of vanadium and successfully applied for the local structural determination of the surface VOₓ species present in supported V₂O₅ catalysts.

Several research groups⁶,⁴⁶–⁴⁷,⁵³ have extended Weber’s methodology to also account for the domain size of the surface WO₆ species present in supported WO₃ catalyst systems. No systematic examination between the UV–vis DRS E₉ values and the number of covalent W=O−W bonds for tungsten oxide compounds, however, has been reported in the literature.

In the present investigation, UV–vis DRS is employed to establish a quantitative correlation between the number of covalent bridging W=O−W bonds in known bulk mixed metal tungstate and polyoxotungstate structures (isolated, polymeric, clusters, and bulk structures) and their corresponding edge energy (E₉).⁹,¹⁰,⁵⁴ This quantitative UV–vis DRS E₉−structure correlation, in conjunction with Raman spectroscopy, is subsequently employed to determine the local molecular structures of the surface tungsten oxide species present in the submonolayer surface coverage region on oxide supports (Al₂O₃, ZrO₂, and SiO₂) under ambient and dehydrated conditions. Unlike other spectroscopic techniques such as Raman and IR that give rise to sharp transitions, UV–vis DRS gives rise to broad bands that tend to overlap for multicomponent systems and only provide an average of the molecular-level characteristics. It is for this reason that complementary Raman and XANES data are required for a complete local structural determination of the
TABLE 1: Bulk Tungstate Reference Compounds

<table>
<thead>
<tr>
<th>bulk tungstate compound</th>
<th>manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum tungstate, Al₂(WO₄)₃</td>
<td>Alfa Aesar, 99%</td>
</tr>
<tr>
<td>ammonium metatungstate, (NH₄)₆H₂W₁₂O₄₄</td>
<td>Pfaltz &amp; Bauer, Inc, 99.5%</td>
</tr>
<tr>
<td>ammonium paratungstate, (NH₄)₁₀H₂W₁₂O₄₀</td>
<td>H.C. Starck, 99%</td>
</tr>
<tr>
<td>calcium tungstate, Ca₂WO₄</td>
<td>Alfa Aesar, 99%</td>
</tr>
<tr>
<td>magnesium tungstate, Mg₂WO₄</td>
<td>Alfa Aesar, 99.5%</td>
</tr>
<tr>
<td>nickel tungstate, Ni₂WO₄</td>
<td>Alfa Aesar, 99%</td>
</tr>
<tr>
<td>phosphotungstic acid, H₃PW₁₂O₄₀H₂O</td>
<td>Aldrich, 99.5%</td>
</tr>
<tr>
<td>potassium tungstate, K₂WO₄</td>
<td>Alfa Aesar, 99%</td>
</tr>
<tr>
<td>silicotungstic acid, H₂SiW₁₂O₄₀H₂O</td>
<td>Aldrich, 99%</td>
</tr>
<tr>
<td>sodium 12-tungstophosphate, Na₆PW₁₂O₄₀</td>
<td>Strem Chemicals, 99%</td>
</tr>
<tr>
<td>sodium tungstate, Na₂WO₄</td>
<td>Alfa Aesar, 98%</td>
</tr>
<tr>
<td>tungsten(VI) oxide, WO₃</td>
<td>Alfa Aesar, 99.8% (metals basis)</td>
</tr>
<tr>
<td>tungsten zirconia, Zr(WO₄)₂</td>
<td>Alfa Aesar, 99.7%</td>
</tr>
<tr>
<td>zinc tungstate, ZnWO₄</td>
<td>Alfa Aesar, 99.7%</td>
</tr>
</tbody>
</table>

surface tungsten oxide species on oxide supports under ambient and dehydrated conditions.

2. Experimental Section

Catalyst Preparation. Most of the bulk tungsten oxide compounds in this study were obtained from commercial suppliers indicated in Table 1, and the compounds were used as received. The bulk metal tungstates of Mg₂W₂O₇, Na₂W₂O₇, and K₂W₂O₇ were prepared by coprecipitation of aqueous ammonium metatungstate, (NH₄)₆H₂W₁₂O₄₄, and the corresponding metal nitrates (Mg(NO₃)₂, 6H₂O, NaNO₃, and KNO₃, Alfa Aesar, 99.9%) with synthesis methods previously reported. Molecular heteropolyoxoantusteggin and Wells-Dawson clusters containing Wₙ₋₁Wₙ⁺(NaH₂SiW₁₂O₄₀H₂O), H₆P₂W₁₈O₆₂H₂O, and K₂[W₉O₃₆]·H₂O were synthesized by methods previously described.

The oxide supports used for this study were Al₂O₃ (Engelhard, S_BET ≈ 200 m²/g), ZrO₂ (Degussa, S_BET = 60 m²/g), and SiO₂ (Cabosil EH-5, S_BET ≈ 330 m²/g). The supported tungsten oxide catalysts were prepared by incipient-wetness impregnation of aqueous solutions of ammonium metatungstate, (NH₄)₆H₂W₁₂O₄₄, 5H₂O (Pfaltz & Bauer, 99.5% purity), and the corresponding metal nitrates (Mg(NO₃)₂, 6H₂O, NaNO₃, and KNO₃, Alfa Aesar, 99.9%) with synthesis methods previously reported.

The oxidative supports were loaded into a single-stage Horiba-Jobin Yvon Lab Ram-HR Raman spectrometer equipped with a confocal microscope (Olympus BX-30) and a notch filter (Kaiser Super Notch). The visible excitation was generated by a Nd−YAG doubled diode pumped laser (Coherent Compass 315M-150; output power of 150 mW with sample power 10 mW), and the UV laser excitation was generated from a He−Cd laser (Kimmon model IK7571-II; output power of 30 mW with sample power ≈ 7 mW). The scattered photons were directed into a single monochromator and focused onto a

200 0.5 0.13
WO₃/ZrO₂ ~200 0.5 0.13
WO₃/SiO₂ ~330 ~0.1 (1%) a

* Monolayer surface coverage for the supported WO₃/SiO₂ catalyst system is not achievable. Maximum dispersion before crystalline WO₃ formation is ~6% WO₃/SiO₂.

UV−vis Diffuse Reflectance Spectroscopy (DRS). The electronic structures of the bulk tungsten oxide reference compounds and the supported tungsten oxide catalysts were obtained with a Varian Cary 5E UV−vis spectrophotometer employing the integration sphere diffuse reflectance attachment (Harrick Praying Mantis Attachment, DRA-2). The finely ground powder samples (~20 mg) of the bulk tungsten oxide reference compounds and the supported tungsten oxide catalysts were loaded into an in situ cell (Harrick, HVC-DR2) and measured in the 200−800 nm region with a magnesium oxide reflectance standard used as the baseline. The UV−vis spectra of the bulk tungsten oxide reference compounds were obtained under ambient conditions, and the spectra of the supported tungsten oxide catalysts were obtained after the samples were treated at 400 °C for 1 h in flowing 10% O₂/He (Airgas, certified, 9.735% O₂/He, ultrahigh purity and hydrocarbon free, 30 mL/min) to desorb the adsorbed moisture, and the spectra of the dehydrated samples were collected after cooling the catalysts back to room temperature in the flowing 10% O₂/He gas. The Raman spectra of the bulk tungsten oxide compounds were taken under ambient conditions. The spectral acquisition time employed was 20 scans of 20 s/spectrum for a total of ~7 min/spectrum.

The UV−vis DRS studies of the supported tungsten oxide catalysts in the present work, absorption from the Al₂O₃ and SiO₂ supports can be neglected as compared to the strong absorption of the W(VI) cations. The ZrO₂ support, however, exhibits strong absorption in the UV−vis region and, thus, cannot be neglected. Therefore, the Al₂O₃, ZrO₂, and SiO₂ supports were used as the baseline for the supported tungsten oxide catalysts to keep all the systems consistent.

The UV−vis spectra were processed with Microsoft Excel software, consisting of calculation of the Kubelka−Monk function, F(R∞), which was extracted from the UV−vis DRS absorbance. The edge energy (Eg) for allowed transitions was determined by finding the intercept of the straight line in the
3. Results

3.1. Bulk Tungsten Oxide Compounds. The Raman spectra of bulk tungsten oxide reference compounds, under ambient conditions, are presented in Figures 1 and 2. The absence of characteristic WO$_3$ vibrations at 805, 715, and 270 cm$^{-1}$ demonstrates the phase purity of these tungstate reference compounds. The corresponding UV–vis DRS band maxima and edge energy values are provided in Table 3. The UV–vis DRS spectra of selected bulk tungstates are shown in Figure 3, which illustrates the various locations of the ligand-to-metal charge transfer (LMCT) transition of different tungsten oxide structures (Figure 3A) and the determination of edge energy from the UV–vis spectra for selected compounds (Figure 3B).

Isolated WO$_4$ Structures. Various bulk crystalline orthotungstate compounds possessing isolated WO$_4$ sites are known (i.e., CaWO$_4$, Na$_2$WO$_4$, K$_2$WO$_4$, Al$_2$(WO$_4$)$_3$, and Zr(WO$_4$)$_2$, etc.). Unfortunately, an ideal WO$_4$ structure has not been found. Hardcastle et al., using the diatomic approximation method, concluded that for an ideal WO$_4$ unit the shortest W–O bond should correspond to a Raman fingerprint located at 874 cm$^{-1}$ ($\nu_3(W=O)$), with a standard deviation of approximately 55 cm$^{-1}$. It is expected for compounds consisting of WO$_4$ units that the $\nu_3$ vibration will shift to higher wavenumber values as the W–O bond is shortened by distortions. The tungstate ion in aqueous solution, [WO$_4$]$^{2-}$, exhibits Raman vibrations at 931 ($\nu_3(W=O)$), 834 ($\nu_4(W=O)$), and 326 (\$\delta(W=O)$) cm$^{-1}$. The shortest W–O bond in the aqueous tungstate ion exhibits a Raman stretching mode at 931 cm$^{-1}$ revealing that the [WO$_4$]$^{2-}$ ion is significantly distorted from the ideal tetrahedron because it is hydroxylated. Bulk CaWO$_4$, which has a scheelite structure, exhibits Raman bands at 910, 838, 796, 395, 320, and 205 cm$^{-1}$, revealing its slightly distorted isolated WO$_4$ unit. Bulk Ni$_2$WO$_4$ consists of a spinel WO$_4$-coordinated structure and exhibits Raman bands at 931, 812, 370, and 308 cm$^{-1}$. The Raman spectrum of the isolated WO$_4$ sites in bulk K$_2$WO$_4$ possesses bands at 925, 850, 823, 350, and 321 cm$^{-1}$. The bulk CuWO$_4$, K$_2$WO$_4$, and Na$_2$WO$_4$ crystalline compounds exhibit a single strong Raman band in the 910–931 cm$^{-1}$ region from the $\nu_3(W=O)$ vibration, reflecting the presence of only one slightly irregular WO$_4$ unit in these reference compounds. The absence of Raman bands in the 500–700 cm$^{-1}$ region reflects the absence of bridging W–O–W bonds in the above structures.

Bulk Al$_2$(WO$_4$)$_3$ and Zr(WO$_4$)$_2$ are more complex tungstates since they contain multiple WO$_4$ sites that are highly distorted. Crystalline Al$_2$(WO$_4$)$_3$ possesses a garnet structure consisting of both regular and distorted WO$_4$ groups that give rise to major Raman features at 1052, 993, 901, 807, 712, 389, 370, and 324 cm$^{-1}$. The bulk Zr(WO$_4$)$_2$ cubic structure exhibits the main Raman features at 1028, 968, 931, 904, 860, 790, 734, 378, 330, 305, 231, and 138 cm$^{-1}$. The appearance of multiple Raman bands in the 900–1060 cm$^{-1}$ range for bulk Al$_2$(WO$_4$)$_3$ and Zr(WO$_4$)$_2$ indicates that these structures contain more than one isolated WO$_4$ unit. The presence of isolated WO$_4$ structures in these orthotungstate reference compounds is confirmed by the absence of Raman features in the 500–700 cm$^{-1}$ range characteristic of bridging W–O–W bonds.

A unique feature of UV–vis DRS for isolated WO$_4$ reference compounds is that they only possess a single ligand-to-metal charge transfer (LMCT) band in the general region of ~218–274 nm, with many of the band maxima occurring at ~220–250 nm. The exact location of this band maximum depends on the extent of distortion of the isolated WO$_4$ structure. For example, K$_2$WO$_4$ has a relatively undistorted isolated WO$_4$ unit and possesses a LMCT band at ~223 nm, whereas Zr(WO$_4$)$_2$ consists of a distorted isolated WO$_4$ unit and exhibits a LMCT band at ~274 nm. The corresponding UV–vis DRS $E_g$ values for the more regular WO$_4$ structures are 5.2–5.6 eV and 4.0–4.2 eV for the highly distorted WO$_4$ structures.

Isolated WO$_4$ Structures. A perfect undistorted isolated WO$_4$ structure has not been found. Hardcastle et al., using the diatomic approximation method, concluded that for an ideal WO$_4$ unit the shortest W–O bond should correspond to a Raman fingerprint located at 874 cm$^{-1}$ ($\nu_3(W=O)$), with a standard deviation of approximately 55 cm$^{-1}$. It is expected for compounds consisting of WO$_4$ units that the $\nu_3$ vibration will shift to higher wavenumber values as the W–O bond is shortened by distortions. The aqueous ion containing an isolated WO$_6$ structure is predicted to give rise to Raman bands at 740 ($\nu_3(W=O)$), 430 ($\nu_4(W=O)$), and 360 (\$\delta(W=O)$) cm$^{-1}$. Unlike an ideal WO$_4$ structure where all normal vibrations are calculated, all four normal vibrational modes of the isolated WO$_4$ site are Raman active, an ideal WO$_6$ structure has multiple WO$_4$ sites that are highly distorted. Crystalline Al$_2$(WO$_4$)$_3$ possesses Raman bands at 925, 850, 823, 350, and 321 cm$^{-1}$. The bulk CuWO$_4$, K$_2$WO$_4$, and Na$_2$WO$_4$ crystalline compounds exhibit a single strong Raman band in the 910–931 cm$^{-1}$ region from the $\nu_3(W=O)$ vibration, reflecting the presence of only one slightly irregular WO$_4$ unit in these reference compounds. The absence of Raman bands in the 500–700 cm$^{-1}$ region reflects the absence of bridging W–O–W bonds in the above structures.

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893 cm\(^{-1}\) is associated with the \(\text{WO}_6\) symmetric stretching vibration. Bulk ZnWO\(_4\) exhibits Raman bands at 906, 782, 707, 676, 541, 510, 404, 336, 311, 270, 189, and 160 cm\(^{-1}\), with the 906 cm\(^{-1}\) band representing the symmetric stretch. Both crystalline \(\text{WO}_6\) structures are distorted, which is reflected in the Raman shift from 691 to 893–906 cm\(^{-1}\) for the symmetric stretch. The corresponding UV–vis DRS \(E_g\) values are \(\sim4.5\) eV with the LMCT band maxima between 247–252 and 342–344 nm, which reflect the distorted nature of the isolated \(\text{WO}_6\) units present in these bulk tungstate reference compounds.

**Dimeric \(\text{W}_2\text{O}_7\) Structure.** Bulk tungsten oxide compounds rarely form polymeric \(\text{WO}_4\) compounds with the exception of...

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**Table 3:** Local \(\text{WO}_6\) Structure and Corresponding UV–vis DRS Edge Energy \((E_g)\) Values of Bulk Tungsten Oxide Reference Compounds

<table>
<thead>
<tr>
<th>Catalyst System</th>
<th>Band Max (nm)</th>
<th>(E_g) (eV)</th>
<th>Mol Struct</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CaWO}_4)</td>
<td>218(sh), 256</td>
<td>5.6</td>
<td>isolated (\text{WO}_4)</td>
</tr>
<tr>
<td>(\text{Na}_2\text{WO}_4)</td>
<td>218, 258 (w)</td>
<td>5.3</td>
<td>isolated (\text{WO}_4)</td>
</tr>
<tr>
<td>(\text{K}_2\text{WO}_4)</td>
<td>223</td>
<td>5.2</td>
<td>isolated (\text{WO}_4)</td>
</tr>
<tr>
<td>(\text{MgWO}_4)</td>
<td>218(sh), 320</td>
<td>4.2</td>
<td>distorted, isolated (\text{WO}_4)</td>
</tr>
<tr>
<td>(\text{Al}_2(\text{WO}_4)_3)</td>
<td>250</td>
<td>4.0</td>
<td>distorted, isolated (\text{WO}_4)</td>
</tr>
<tr>
<td>(\text{Zr}(\text{WO}_4)_2)</td>
<td>274</td>
<td>4.5</td>
<td>distorted, isolated (\text{WO}_6)</td>
</tr>
<tr>
<td>(\text{NiWO}_4)</td>
<td>247(sh), 342</td>
<td>4.5</td>
<td>distorted, isolated (\text{WO}_6)</td>
</tr>
<tr>
<td>(\text{ZnWO}_4)</td>
<td>270(w), 344</td>
<td>4.3</td>
<td>dimeric (\text{O}_2\text{W}--\text{O}--\text{WO}_3)</td>
</tr>
<tr>
<td>(\text{Na}_2\text{WO}_4)</td>
<td>252, 296 (w)</td>
<td>4.1</td>
<td>infinite chain, alternating (\text{WO}_4/\text{WO}_6)</td>
</tr>
<tr>
<td>(\text{K}_2\text{WO}_4)</td>
<td>250, 270(w)</td>
<td>3.6</td>
<td>infinite chain, alternating (\text{WO}_4/\text{WO}_6)</td>
</tr>
<tr>
<td>(\text{Al}_2(\text{WO}_4)_3)</td>
<td>252, 306(w)</td>
<td>3.7</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\text{Na}_2\text{HSiW}<em>9\text{O}</em>{34})</td>
<td>250, 294(sh)</td>
<td>3.6</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{H}_2\text{W}<em>3\text{O}</em>{12})</td>
<td>269, 314</td>
<td>3.5</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{H}_2\text{W}<em>3\text{O}</em>{12})</td>
<td>254, 318</td>
<td>3.5</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\alpha-K_2\text{WO}_3\cdot\text{H}_2\text{O})</td>
<td>290</td>
<td>3.4</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\text{H}_2\text{SiW}<em>12\text{O}</em>{38})</td>
<td>254, 323</td>
<td>3.4</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\text{H}_2\text{P}_2\text{W}<em>2\text{O}</em>{10}\cdot2\text{H}_2\text{O})</td>
<td>254, 306</td>
<td>3.4</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\text{Na}_3\text{PW}<em>12\text{O}</em>{40})</td>
<td>255, 328</td>
<td>3.4</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\alpha-K_2\text{P}_2\text{W}<em>6\text{O}</em>{12}\cdot10\text{H}_2\text{O})</td>
<td>257(sh), 302, 345, 372(sh)</td>
<td>3.1</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\text{Na}_2\text{PW}<em>12\text{O}</em>{40}\cdot2\text{H}_2\text{O})</td>
<td>255(sh), 300(w), 356, 384</td>
<td>3.0</td>
<td>(\text{WO}_6)-containing cluster</td>
</tr>
<tr>
<td>(\text{WO}_3)</td>
<td>251, 330</td>
<td>2.8</td>
<td>infinite 3D (\text{WO}_6) structure</td>
</tr>
</tbody>
</table>
MgW₂O₇ that consists of a pair of sharing WO₄ tetrahedra (dimeric O₃W−O−WO₃ unit). The Raman bands of bulk MgW₂O₇ appear at 980, 920, 967, 790, 712, 551, 516, 420, 370, 350, 274, 240, and 176 cm⁻¹. The 980 cm⁻¹ vibration represents the v₁(ν(W=O)), the vibrations in the 500–800 cm⁻¹ range represent v₂(W−O−W) and v₃(W−O−W), and the δ(W−O) and δ(W−O−W) bending modes occur in the 200–400 cm⁻¹ range. Two LMCT band maxima at 252 and 296 (w) nm are present in the UV−vis spectrum of MgW₂O₇. The corresponding UV−vis DRS E₃g value of 4.3 eV is slightly lower than that found in the isolated WO₄ or WO₆ bulk compounds with the exception of the highly distorted isolated WO₄ structures.

Polymeric W₂O₇ Linear Chain. Bulk disodium tungstate, Na₂W₂O₇, and dipotassium tungstate, K₂W₂O₇, are composed of alternating WO₄ and WO₆ units joined to give an infinite polymeric chain. The Raman band at 934−933 cm⁻¹ is assigned to the symmetric W=O stretching mode of the WO₄ site, and the band at 888−876 cm⁻¹ is assigned to the symmetric W=O stretching mode of the WO₆ site. The stretching and bending modes of the bridging W=O−W infinite chain appear at ~500−800 and ~200−300 cm⁻¹, respectively. The UV−vis spectrum of Na₂W₂O₇ gives rise to two LMCT bands with maxima at 250 and 270 nm, and the UV−vis spectrum of K₂W₂O₇ also gives rise to two LMCT bands with maxima at 252 and 306 nm. The corresponding UV−vis DRS E₃g values for Na₂W₂O₇ and K₂W₂O₇ of 4.1 and 3.6 eV, respectively, are lower than that found in the dimeric O₃W−O−WO₃ structure as well as the isolated WO₄ or WO₆ reference compounds. The E₃g value for Na₂W₂O₇, however, exhibits a comparable E₃g value also found for highly distorted and isolated WO₄ structures (i.e., Al₃(WO₄)₃ and Zr(WO₄)₂), whereas the E₃g value for K₂W₂O₇ lies much lower.

W₂O₇−W₁O₆ Clusters. Tungsten oxide clusters composed of polymeric WO₆ units are found in ammonium tungstates as well as Wells-Dawson and Keggin heteropolytungstate compounds. Ammonium metatungstate, [W₁₂O₃₉(NH₄)₁₂]⁻², possesses significantly distorted WO₆ units and exhibits Raman features at ~796 (v₁(W=O)), 958, 930, 834 (v₄(W=O)), and W−O−W modes at 700−500 and 330−190 cm⁻¹. The Keggin heteropolyoxo anions consist of polymeric W₁₂O₆O₆ clusters with the general formula of [X₂W₁₀O₃₇]⁻³. The Keggin anion’s general structure is composed of a globe-like cluster of corner and edge-sharing WO₆ units that enclose a central XO₄ unit (where X represents P, Si, etc.). The tungsten WO₆ units possess one short W=O bond, four W−O−W bonds, and one long W−O−X bond to the central XO₄ unit. The Raman spectra of the Keggin anions exhibit bands between 950 and 1015 cm⁻¹ (ν₁(W=O)) and 825−930 cm⁻¹ (ν₄(W=O)) as well as bands at lower wavenumbers arising from the bridging W−O−W bonds. The larger Wells-Dawson heteropoly anions, (i.e., α-[X₃W₁₈O₆₀]⁺⁻) and Wells-Dawson lacunary species (i.e., α-[X₃W₁₇O₆₁]⁺⁻) exhibit multiple W=O vibrations between 950 and 1005 cm⁻¹, reflecting a distribution of distortions among the WO₆ units in the framework.

The corresponding UV−vis DRS E₃g values for these reference isopolytungstates occur between 3.0 and 3.6 eV, which is much lower than any of the previous tungsten oxide reference compounds. These isopolytungstate compounds contain multiple LMCT transitions which differ slightly depending on the parent ion. For the Keggin compounds with the general formula [X₂W₁₀O₃₇]⁻³, two LMCT transitions occur between 250−269 and 294−328 nm. The larger Wells-Dawson heteropoly anions, (i.e., α-[X₃W₁₈O₆₀]⁺⁻) possess a single LMCT transition at 290 nm, where the Wells-Dawson lacunary species (i.e., α-[X₃W₁₇O₆₁]⁺⁻) exhibit four LMCT transitions between 247 and 257, ~300, 345−356, and 372−384 nm. Furthermore, the position of the UV−vis DRS band maxima and the E₃g values of the Keggins are independent of the central cation (Si or P) as well as the charge-balancing secondary cation (H⁺ or Na⁺).

Infinite 3D Structure. Crystalline WO₃ is a three-dimensional structure composed of distorted WO₄ units that exhibits major Raman bands at 805, 715, and 270 cm⁻¹. The 805 and 715 cm⁻¹ vibrations arise from the bridging W−O−W stretching frequencies, and the 270 cm⁻¹ vibration is the related bridging W−O−W bending mode. Bulk WO₃ contains two LMCT transitions at 251 and 338 nm with the corresponding UV−vis DRS E₃g value of 2.8 eV which is even lower than that found for the finite clusters present in the Keggin and Wells-Dawson reference compounds. Crystalline WO₃ nanoparticles (NPs) give rise to strong Raman bands, and the absence of these bands in the tungsten oxide reference compounds reflects their phase purity.

Summary of UV−vis and Raman Spectroscopy of Bulk Tungstates. The extensive set of UV−vis and Raman spectra in Figures 1 and 2 and Table 3 reveal several trends between tungstate structures and their spectra. Raman spectroscopy is sensitive to (i) the number of distinct WO₄ sites in a structure (reflected in the number of symmetric bands in the high wavenumber region), (ii) the extent of distortion of the local WO₄ structure (shift in symmetric stretch relative to ideal structures), and (iii) the presence of the polytungstate functionality (W−O−W). Furthermore, the Raman bands tend to be sharp, and the molecular nature of Raman spectroscopy sometimes allows identification of specific structures when appropriate reference compounds are available. A minor downside of Raman spectroscopy is that it is more sensitive to species possessing higher W−O bond order (i.e., W=O vs W−O).

The UV−vis spectra allow for discrimination between mildly distorted isolated WO₄/WO₆ (E₃g > 4.4 eV) and polymeric structures (E₃g < 4.0 eV). The number and location of LMCT transition band maxima further discriminates between these structures since isolated WO₆ units generally result in only one strong transition occurring at ~220 nm, whereas slightly distorted monotungstate structures and polytungstates, especially clusters, tend to give rise to multiple strong LMCT bands between 250 and 350 nm. In the region 4.0 eV < E₃g < 4.4 eV, however, several types of tungstate compounds possess E₃g values that complicate UV−vis structural assignments. For example, highly distorted WO₆ sites give rise to E₃g values of 4.0−4.2 eV with an LMCT of ~250−270 nm, the dimeric W₂O₇ unit exhibits an E₃g value of 4.3 eV with LMCT of ~250 nm, and polytungstate W₂O₇ chains can also yield an E₃g value of 4.1 eV with an LMCT of ~250 nm.

A further complication of UV−vis spectral analysis can result when multiple structures are present in the same sample because of the breadth of the bands. For example, if a mixture contains comparable quantities of both mildly distorted WO₄ species (Na₂WO₄ with E₃g ~ 5.3 eV and LMCT ~ 218 nm) and highly distorted WO₆ species (Al₃(WO₄)₃ with E₃g ~ 4.2 eV and LMCT ~ 250 nm), the resulting UV−vis spectrum is dominated by the lower E₃g value of the highly distorted WO₆ species and exhibits two LMCT band maxima at 218 and 255 nm (see Figure 3C). Note that the apparent E₃g value of the Na₂WO₄/Al₃(WO₄)₃ physical mixture is dominated by the lower E₃g value of the highly distorted WO₆ site present in Al₃(WO₄)₃, but the LMCT transition gives rise to the two bands from the individual Na₂WO₄ and Al₃(WO₄)₃ structures. A similar result would occur if
a sample has comparable amounts of monotungstate and polytungstate components. For multicomponent tungstate systems, thus, the overall $E_g$ value is dominated by the component with lowest $E_g$ values and the LMCT transition of each component is retained. The broad nature of the UV–vis LMCT bands, however, sometimes complicates detection of each individual LMCT transition in mixed tungstate structures. It is, thus, critical that both Raman and UV–vis spectra be collected on the same sample and under the same experimental conditions to obtain a more complete perspective of the components in tungstate mixtures.

3.2. Supported Tungsten Oxide Catalysts. The surface tungsten oxide coverage and loading for the examined supported WO$_3$ catalysts are summarized in Table 2. Monolayer surface coverage for Al$_2$O$_3$ and ZrO$_2$ is $\sim$4.5 W atoms/nm$^2$.40,70,71 The maximum dispersion achieved for the supported WO$_3$/SiO$_2$ catalyst is $\sim$0.5 W atoms/nm$^2$ since higher tungsten oxide loadings resulted in the presence of crystalline WO$_3$ NPs. The Raman spectra under ambient and dehydrated conditions of the supported WO$_3$ catalysts are shown in Figures 4–6, and the corresponding UV–vis DRS edge energies and LMCT transitions are listed in Tables 4 and 5.

Supported WO$_3$/Al$_2$O Catalysts. The Raman spectra of the supported WO$_3$/Al$_2$O$_3$ catalysts under ambient and dehydrated conditions are presented in Figure 4. The Al$_2$O$_3$ support does not give rise to any Raman vibrations, which allows detection of all of the W–O vibrations. Raman bands from crystalline WO$_3$ NPs (805, 715, 270 cm$^{-1}$) are not present and confirm the successful complete dispersion of the tungsten oxide phase over the Al$_2$O$_3$ support at high and low surface coverage. Under ambient conditions, Raman bands are present at $\sim$990 cm$^{-1}$ $\nu_9$(W=O) and $\sim$867 cm$^{-1}$ $\nu_6$(W=O) for the hydrated monolayer supported 4.5WAl sample that are characteristic of the hydrated [W$_{12}$O$_{39}$]$^{6-}$ cluster that possesses Raman bands at $\sim$990–960 cm$^{-1}$ ($\nu_9$(W=O)) and 330–190 cm$^{-1}$ (W–O–W mode).31,74 Sample fluorescence prevented collection of the Raman spectra for the low-coverage supported 0.5WAl catalyst under ambient conditions, but a previous Raman analysis of supported 0.5WAl catalyst under ambient conditions exhibited bands at 951, 880, and 330 cm$^{-1}$.31 These vibrations are characteristic of distorted aqueous [WO$_4$]$^{2-}$ monotungstate.31 Upon dehydration, the major Raman bands from the dehydrated surface WO$_3$ species appear at $\sim$1001 and 1015 cm$^{-1}$ for the supported 0.5 and 4.5WAI catalysts, respectively. The monolayer supported 4.5WAI catalyst contains additional Raman bands at $\sim$867, $\sim$780, and $\sim$323 cm$^{-1}$ assigned to the symmetric stretch of the bridging W=O–Al bond, asymmetric stretch of the bridging W=O–W bond, and associated O–W–O bending mode of the dehydrated surface WO$_3$ species, respectively.29,30,72 The short W=O bonds at $\sim$1001 and $\sim$1015 cm$^{-1}$ are
TABLE 4: Comparison of UV−vis DRS Local WO₃ Molecular Structural Assignments for Supported WO₃ Catalysts with Raman and XANES under Ambient Conditions

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>band max (nm)</th>
<th>$E_g$ (eV)</th>
<th>average no. W−O−W bonds</th>
<th>UV−vis DRS</th>
<th>Raman</th>
<th>XANES</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 W/nm² WO₃/Al₂O₃</td>
<td>227</td>
<td>5.3</td>
<td>~0</td>
<td>mononitrate (WO₃)</td>
<td>polytungstate (HW₆O₂₁)³⁻</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>4.5 W/nm² WO₃/Al₂O₃</td>
<td>228, 254</td>
<td>4.1</td>
<td>2.2</td>
<td>combination of mononitrate and polytungstates</td>
<td>polytungstate [W₁₂O₃₉]⁶⁻</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>0.5 W/nm² WO₃/ZrO₂</td>
<td>226, 249</td>
<td>4.6</td>
<td>1.1</td>
<td>mononitrate (WO₃)²⁻</td>
<td>polytungstate [HW₆O₂₁]³⁻</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>4.5 W/nm² WO₃/ZrO₂</td>
<td>221, 249, 266 (sh)</td>
<td>4.3</td>
<td>1.6</td>
<td>combination of mononitrate and polytungstates</td>
<td>polytungstate [W₁₂O₃₉]⁶⁻</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>~0.1 W/nm² WO₃/SiO₂</td>
<td>224, 260</td>
<td>4.2</td>
<td>2.0</td>
<td>combination of mononitrate and polytungstates</td>
<td>polytungstate [W₁₂O₃₉]⁶⁻</td>
<td>Si-containing Keggin-type cluster</td>
</tr>
<tr>
<td>~0.5 W/nm² WO₃/SiO₂</td>
<td>222, 260</td>
<td>4.2</td>
<td>2.1</td>
<td>combination of mononitrate and polytungstates</td>
<td>polytungstate [W₁₂O₃₉]⁶⁻</td>
<td>Si-containing Keggin-type cluster</td>
</tr>
</tbody>
</table>

TABLE 5: Comparison of UV−vis DRS Local WO₃ Molecular Structural Assignments for Supported WO₃ Catalysts with Raman and XANES under Dehydrated Conditions

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>band max (nm)</th>
<th>$E_g$ (eV)</th>
<th>average no. W−O−W bonds</th>
<th>UV−vis DRS</th>
<th>Raman</th>
<th>XANES</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 W/nm² WO₃/Al₂O₃</td>
<td>228</td>
<td>5.1</td>
<td>~0</td>
<td>mononitrate (WO₃)</td>
<td>polytungstate (monoxo WO₅)</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>4.5 W/nm² WO₃/Al₂O₃</td>
<td>234, 254</td>
<td>4.0</td>
<td>2.5</td>
<td>combination of mononitrate and polytungstates</td>
<td>polytungstate (monoxo WO₅)</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>0.5 W/nm² WO₃/ZrO₂</td>
<td>219, 240, 251(sh)</td>
<td>5.0</td>
<td>0.1</td>
<td>mononitrate (WO₃)²⁻</td>
<td>polytungstate (monoxo WO₅)</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>4.5 W/nm² WO₃/ZrO₂</td>
<td>218, 246, 268 (sh)</td>
<td>4.2</td>
<td>1.9</td>
<td>combination of mononitrate and polytungstates</td>
<td>polytungstate (monoxo WO₅)</td>
<td>distorted WO₃/WO₆</td>
</tr>
<tr>
<td>~0.1 W/nm² WO₃/SiO₂</td>
<td>228, 261</td>
<td>4.2</td>
<td>2.0</td>
<td>mononitrate or combination of mononitrate and polytungstates</td>
<td>polytungstate (dioxo WO₄)</td>
<td>N/A</td>
</tr>
<tr>
<td>~0.5 W/nm² WO₃/SiO₂</td>
<td>235, 270</td>
<td>4.0</td>
<td>2.4</td>
<td>mononitrate or combination of mononitrate and polytungstates</td>
<td>polytungstate (dioxo WO₄)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

characteristic of monoxo-containing surface WO₃ mononitrate and surface WO₃/WO₆ polytungstates, respectively.⁹⁹

The corresponding UV−vis DRS $E_g$ values under ambient and dehydrated conditions for the 0.5 WAl sample are ~5.3 and ~5.1 eV, respectively, which are similar in value for reference compounds containing isolated WO₃ units (i.e., Na₂WO₄, Table 3).⁶¹ The presence of only a single LMCT band maximum at 227−228 nm confirms the isolated nature of the supported WO₃ units. The UV−vis DRS $E_g$ values under ambient and dehydrated conditions for the 0.5 WAl sample are ~4.1 and ~4.0, respectively, and similar to the values found for tungstate reference compounds consisting of either tungstate WO₄ chains (i.e., Na₃WO₄, alternating WO₃ and WO₄ units, Table 3),⁶¹ highly distorted isolated WO₃ species (i.e., Al₅(WO₄)₃ and Zr(WO₄)₃), or a mixture of mononitrate and polytungstates. Multiple LMCT transitions are observed for the 4.5WAl sample at ~228−234 and ~254 nm under hydrated and dehydrated conditions. The low value of the LMCT transitions at ~228−234 nm reflects the presence of a slightly distorted isolated surface WO₃ species, and the additional band at ~254 nm is representative of either a highly distorted mononitrate WO₃ species or a polytungstate species, with the latter more likely.

The combined Raman and UV−vis spectroscopic information suggests the following supported tungstate structures on Al₂O₃ under ambient and dehydrated conditions. The surface WO₃ species on Al₂O₃ at low coverage is a slightly distorted mononitrate species under both hydrated ([WO₄]³⁻) and dehydrated (O₃W≡O) conditions. Note that the UV−vis spectral features for such a reference structure are not contained in Table 3 because such a reference compound was not obtained. The hydrated surface WO₃ species on Al₂O₃ at monolayer coverage are present as mononitrate [WO₄]²⁻ and polytungstate [W₁₂O₃₉]⁶⁻ clusters. The dehydrated surface WO₃ species on Al₂O₃ at monolayer coverage are present as both mononitrate and polytungstate WO₃/WO₆ species possessing the monoxo W−O functionality.

Supported WO₃/ZrO₂ Catalysts. The Raman spectra of the supported WO₃/ZrO₂ catalysts under ambient and dehydrated conditions are shown in Figure 5. The ZrO₂ (monoclinic) support possesses strong Raman bands at ~640, ~615, ~558, ~535, ~475, ~380, ~330, ~267, and ~125 cm⁻¹ that interfere with the detection of the Raman bands for tungstate vibrations that occur below ~700 cm⁻¹. Fortunately, no ZrO₂ Raman bands are present in the critical 700−1100 cm⁻¹ region where the W=O vibrations for the supported tungsten oxide species occur. A small Raman band from trace amounts of crystalline WO₃ NPS at 816 cm⁻¹ is only present in the spectra for the dehydrated 4.5WZr catalyst sample, which reflects the good dispersion of the tungsten oxide phase on the ZrO₂ support. Under ambient conditions where the surface is hydrated, the Raman spectra of the supported 0.5 and 4.5 WZr catalysts exhibit bands at ~945 and ~955 cm⁻¹ due to the symmetric stretching mode of the hydrated surface WO₃ species.⁷⁸,⁷⁹ The hydrated Raman band at ~945 cm⁻¹ at low surface coverage is characteristic of aqueous distorted [WO₄]²⁻, and the band at ~955 cm⁻¹ is most probably a combination of distorted aqueous [WO₄]²⁻ and aqueous [HW₆O₂₁]³⁻ paratungstate.⁸⁰ Upon dehydration the major Raman bands associated with the surface tungsten oxide species become sharp and shift from ~900 to ~1010 cm⁻¹ with surface WO₃ coverage. The appearance of the short W=O bonds at ~1000 and 1010 cm⁻¹ are characteristic of dehydrated surface WO₃ mononitrate and surface WO₃/WO₆ polytungstate species, respectively.⁸⁰,⁸⁸,⁸⁹ An additional Raman band is present at ~915 cm⁻¹ for the dehydrated monolayer 4.5 WZr catalyst samples from the bridging W−O−Zr bond.⁹⁹

The corresponding UV−vis DRS $E_g$ values under ambient and dehydrated conditions for the 0.5WZr catalyst sample are...
The dehydrated 0.5WZr catalyst sample $E_g$ value corresponds to isolated WO$_4$ species (see Table 3) or possibly isolated WO$_3$ species. The corresponding UV−vis DRS $E_g$ values under ambient and dehydrated conditions for the 4.5WZr sample are $\sim$4.3 and $\sim$4.2 eV, respectively, which is similar to the value found for reference compounds consisting of polymeric WO$_4$ chains (i.e., Na$_3$W$_2$O$_7$ with alternating WO$_4$ and WO$_6$ units in Table 3),$^{46}$ dimeric W$_2$O$_7$(i.e., MgW$_2$O$_7$ in Table 3), highly distorted isolated species (i.e., Zr(WO$_4$)$_2$ in Table 3), or even a mixture of slightly distorted WO$_4$ and polytungstate. The appearance of multiple LMCT transitions at $\sim$221−226 and 249 nm under ambient conditions and LMCT transitions at $\sim$219, 240−246, and 251−264(sh) suggests that both monotungstate and polytungstate species are present for 4.5WZr under all conditions.

The combined Raman and UV−vis spectroscopic information suggests the following supported tungstate structures on ZrO$_2$ under ambient and dehydrated conditions. Under ambient conditions, only hydrated isolated [WO$_4$]$_2^{2−}$ species are present at low coverage and hydrated [WO$_4$]$_2^{2−}$/[HW$_6$O$_21$]$_5^{5−}$ species are present at monolayer coverage. Under dehydrated conditions, isolated surface O$_4$W=O monotungstate is found at low coverage and surface WO$_4$/WO$_3$ polytungstate species are present at monolayer coverage.

**Supported WO$_3$/SiO$_2$ Catalysts.** The Raman spectra of the supported WO$_3$/SiO$_2$ catalysts under ambient and dehydrated conditions are presented in Figure 6. The SiO$_2$ support possesses weak Raman bands at $\sim$802, $\sim$605, $\sim$490, and $\sim$400−$\sim$1 cm$^{-1}$ originating from vibrations of 2-, 3-, and 4-membered silica rings and a band at $\sim$975 cm$^{-1}$ which is associated with the Si−OH vibration.$^{68,73}$ A trace amount of WO$_3$ NPs is present for the hydrated 0.5WSi catalyst sample as revealed by the weak Raman bands at $\sim$807 and $\sim$713 cm$^{-1}$, which reflects the high dispersion of the tungsten oxide phase on the SiO$_2$ support under hydrated and dehydrated conditions. Under ambient conditions, Raman bands appear at $\sim$966 cm$^{-1}$ with accompanying bands at lower wavenumbers for the 0.1 and 0.5 WSi catalysts originating from the hydrated [W$_{12}$O$_{39}$]$^{6−}$ clusters that have been previously identified on hydrated SiO$_2$ supports.$^{29,72}$ These bands are probably slightly shifted to higher wavenumber values because of the contribution of the of the Si−OH vibration at $\sim$975 cm$^{-1}$. Upon dehydration, the surface WO$_4$ species give rise to strong Raman bands at 981−985 and 1015 cm$^{-1}$, with the latter only present for the supported 0.5WSi catalyst. The Raman bands between 980 and 990 cm$^{-1}$ are consistent with a dehydrated isolated surface WO$_4$ structure with dioxo O=O coordinated species.$^{89}$ The Raman band at 1015 cm$^{-1}$ is characteristic of monoxo W=O surface WO$_3$ coordinated species$^{89}$ with the weak band at $\sim$346 cm$^{-1}$ assigned to the bending mode of the dehydrated surface WO$_3$/WO$_4$ species.

The corresponding UV−vis DRS $E_g$ values for the ambient 0.1 and 0.5WSi are both 4.2 eV, and upon dehydration the $E_g$ values remains about the same (4.0−4.2 eV). Under hydrated conditions, both samples contain two LMCT transition at $\sim$224 and 260 nm, whereas upon dehydration the LMCT transitions slightly shift to 228−235 and 261−270 nm, respectively. Both the LMCT band maxima and the $E_g$ values suggest that the surface tungstate consists of distorted isolated WO$_4$ dioxo surface species as well as polytungstate monoxo surface WO$_3$/WO$_4$ species.

**4. Discussion**

**Correlation of the UV−vis DRS $E_g$ with the Local Structures of W(VI) Oxides.** The UV−vis DRS edge energies of V(V) and Mo(VI) cations have previously been successfully correlated with the number of M−O−M bonds or the local symmetry of the central cation.$^{50,52}$ Qualitatively, the UV−vis DRS edge energies of the W(VI) cation have also been found to be sensitive to the local coordination geometry and cations in the second coordination sphere.$^{9,10,53}$ Following the previous successful empirical correlations between $E_g$ and the number of nearest cations surrounding the central M cation, a correlation between $E_g$ and the average number of covalent bridging W−O−W bonds ($N_{W-O-W}$) of the central W(VI) cation is also examined for the W(VI)-containing tungsten oxide reference compounds of this paper. The plot of $E_g$ vs $N_{W-O-W}$ is presented in Figure 7, where the $E_g$ values linearly vary inversely with $N_{W-O-W}$ with the exception of the isolated WO$_3$ structures whose $E_g$ values vary over a wide range ($\sim$4.0−5.6 eV), which is similar to the earlier correlation for V(V) compounds.$^{50}$ These relationships are quite similar to the number of nearest metal neighbors ($N_M$) proposed by Weber$^{52}$ for Mo(VI) compounds, which represents the degree of aggregate/polymerization of the absorbing species. The line shown in Figure 7 can be expressed by the equation

$$N_{W-O-W} = 11.89 - 2.37E_g$$

with $R^2 = 0.9496$ (1)

The high $R^2$ value is attributed to the distribution of $E_g$ values for the isolated WO$_3$/WO$_4$ structures over a wide range ($\sim$4.0−
5.6 eV) due to the distortion of the isolated WO₄ structures. The obtained W(VI) correlation is comparable to that obtained by Weber for Mo(VI) oxides, \( N_{Mo} = 16 - 3.8E_g \), and Gao et al. for V(V) oxide clusters, \( N_{V} - O - V = 14.03 - 3.95E_g \). The similar correlations obtained for the W(VI), Mo(VI), and V(V) cations suggest that the edge energies of metal oxide clusters are associated with the extent of spatial delocalization of the molecular orbitals involved with electronic transitions, as initially proposed by Weber.²² It follows from the correlation in Figure 7 that \( E_g \) is primarily determined by the number of covalent bridging W≡O=W bonds or the degree of polymerization of the central W(VI) cation. The wide range of \( E_g \) values obtained for the isolated WO₄/WO₆ structures appears to reflect the sensitivity of the UV−vis DRS measurement to the extent of distortion of W(VI) cation and needs to be considered when determining local structures.

An inverse relationship between \( E_g \) and domain size or number of WO₃ units in a tungsten oxide cluster has also recently been invoked in the literature¹⁰,⁴₀,⁴₆,⁷₆ but never been rigorously examined. The plot of \( E_g \) versus \( N_W \), where \( N_W \) represents the number of W atoms present in a finite cluster, is presented in Figure 8. The \( E_g \) vs \( N_W \) plot does not support a direct relationship between \( E_g \) and \( N_W \) or domain size for finite WO₃ clusters as shown by the plot in Figure 8. First, the \( E_g \) values for isolated WO₃/WO₆ structures vary over a very wide range due to the sensitivity to extent of distortion of the W(VI) cation. Second, comparable \( E_g \) values are obtained for finite WO₃/WO₆ clusters and infinite linear chains. Third, both crystalline WO₃ NPs and polymeric W₆O₁₉ linear chain structures are infinite but exhibit widely varying \( E_g \) values. The inverse relationship between \( E_g \) and \( N_{W-O-W} \) better captures the variation of the UV−vis DRS \( E_g \) values with the local structure of the W(VI) cation.

**Surface Structures of Supported Tungsten Oxide Catalysts.** The \( E_g \) vs \( N_{W-O-W} \) correlation implies that the edge energies of the supported tungsten oxide species can also be used to estimate the local WO₃ surface structures. The average \( N_{W-O-W} \) for the supported tungsten oxide catalysts can be calculated based on the empirical equation obtained above, \( N_{W-O-W} = 11.89 - 2.37E_g \), and the results are listed in Tables 4 and 5 with the UV−vis DRS possible structural assignments. However, since the \( E_g \) values tend to be rather complex when multiple structures are present, it is necessary to also include the LMCT transitional bands when making structural assignments as well as employ complementary structural characteriza-

**Supported WO₃/Al₂O₃ Catalysts.** For the hydrated supported 0.5WAl catalyst, <15% monolayer coverage, the current UV−vis and Raman are in agreement with each other and XANES structural studies conducted by Horsley et al.,²⁵ Eibl et al.,²² and Hilberg et al.²¹ concluding hydrated WO₃ coordinated monotungstate units are present (see Table 4). For the hydrated supported 4.5 WAl monolayer catalyst, the current UV−vis and Raman and previous XANES studies are also in agreement that distorted square pyramidal (WO₃) or pseudo-octahedral (WO₆) structures are the predominant species (see Table 4), with Raman indicating the presence of hydrated \([W_12O_{39}]^{6−}\) polytungstate species. UV−vis analysis also suggests the presence of some monotungstate species.

Under dehydrated conditions, all spectroscopic characterization studies are in agreement that isolated surface tungstate species are present for dehydrated 0.5WAl (see Table 5). Raman analysis suggests that the surface monotungstate species possess monoxo W≡O functionality (O≡W≡O). The presence of dehydrated surface WO₃/WO₆ polytungstate species are concluded for the 4.5WAl catalyst sample from all spectroscopic methods (see Table 5) with the additional observation of isolated monotungstate species from UV−vis DRS.

**Supported WO₃/ZrO₂ Catalysts.** The assigned tungstate surface structures on the ZrO₂ support are also in agreement with Raman, UV−vis, and earlier XANES²² spectroscopic measurements and almost the same as those found above for the supported WO₃/Al₂O₃ catalysts (see Tables 4 and 5). The hydrated polytungstate \([HW(AlO_2)]^{5−}\), however, is found at monolayer coverage on ZrO₂, while the hydrated \([W_{12}O_{39}]^{6−}\) is found for the comparable Al₂O₃ catalyst because of the different pH at point of zero charge (PZC) values of the hydrated supports.

**Supported WO₃/SiO₂ Catalysts.** Unlike WO₃ supported on ZrO₂ and Al₂O₃ where the catalyst edge energy and average \( N_{W-O-W} \) values are a strong function of the tungsten oxide loading, this does not hold true for supported WO₃/SiO₂. The supported 0.1WSi and 0.5WSi catalysts exhibit intermediate edge energies of 4.2 eV under ambient conditions and 4.0−4.2 eV under dehydrated conditions, reflecting \( N_{W-O-W} \) values of ~2.0 and ~2.0−2.4, respectively. The UV−vis DRS possesses multiple LMCT transitions at ~222 and 260 nm under ambient conditions and ~228−235 and 261−270 nm under dehydrated conditions. Comparison with reference compounds suggests that on the SiO₂ surface highly distorted isolated surface WO₃ are the predominate species (i.e., Al₅(WO₃)₃ and NiWO₃ contain distorted WO₃ and WO₆ units, see Table 3).²⁶ The correlation results, however, also suggest that the surface WO₃ species could lie within the polymeric region. It is for this reason that complementary characterization techniques must be used to verify the molecular species present. In the present study under ambient conditions Raman bands appear at ~966 cm⁻¹ with accompanying bands at lower wavenumbers for the 0.1 and 0.5 WSi catalysts originating from hydrated \([W_12O_{39}]^{6−}\) clusters that have been previously identified on hydrated SiO₂ supports.²₉,₃₁,₇₄ The presence of some hydrated \([WO_4]^{2−}\) is also suggested from UV−vis DRS.

Upon dehydration, the surface WO₃ species give rise to strong Raman bands at 981−985 and 1015 cm⁻¹, with the latter only present for the supported 0.5WSi catalyst. The Raman band at 981−985 cm⁻¹ is consistent with a dehydrated isolated surface WO₃ structure with dioxo O=W=O coordinated species.²⁹ The Raman band at 1015 cm⁻¹ is consistent with monoxo W≡O
surface WO₃/WO₅ coordinated species with the weak band at \( \sim 346 \text{ cm}^{-1} \) assigned to the bending mode of the dehydrated surface WO₃/WO₅ species.

Recent EXAFS studies of supported WO₃/SiO₂ under ambient conditions proposed that either hydrated polytungstate chains or dodecatungstosilicate Keggin clusters are present. Other researchers also detected small amounts of dodecatungstosilicic acid in hydrated supported WO₃/SiO₂ catalysts when prepared via wet impregnation. Hydrated \( \text{H}_2\text{SiW}_12\text{O}_{40} \) clusters would also give rise to two LMCT bands with an edge energy of \( \sim 3.4 \text{ eV} \), which are not observed for the present hydrated supported WO₃/SiO₂ catalysts.

5. Conclusions

The UV–vis DRS spectroscopic method, with the aid of Raman spectroscopy, was utilized to study the surface structures of molecularly dispersed tungsten(VI) oxide on oxide supports (\( \text{Al}_2\text{O}_3, \text{ZrO}_2, \text{and SiO}_2 \)) under ambient and dehydrated conditions. Under ambient conditions, hydrated surface \([\text{WO}_4]^{2-}, [\text{HW}_2\text{O}_5]^{3-}\), and \([\text{W}_12\text{O}_{40}]^{6-}\) species were found to be present on the supports, and their relative concentration depends on the surface coverage and pH at PZC of the oxide support. At low surface coverage and dehydrated conditions, isolated surface \( \text{OW}_2\text{O}_2 \) monoxygeno species are present on \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \), and isolated surface \( \text{OW}=(\text{O})\text{O}_2 \) dioxygeno species are present on \( \text{SiO}_2 \). At high surface coverage under dehydrated conditions, monotonostate surface \( \text{OW}_2\text{O} \) and polytungstate \( \text{W}_6\text{O}_{18} \) species are present on \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) and monotonostate surface \( \text{OW}=(\text{O})_2 \) and monoxygeno surface \( \text{WO}_3\text{WO}_5 \) species on \( \text{SiO}_2 \). The current study demonstrates that the combination of UV–vis DRS and Raman spectroscopy allows discrimination between surface monotonostate and polytungstate structures as well as WO₃ NPs.

On the basis of various tungsten oxide reference compounds, a correlation of \( \text{NWO}_2=(1.189−2.37E_g) \) was established between the edge energy, \( E_g \), and the average number of covalent W–O–W bonds around the central W(VI) cations. A direct relationship between \( E_g \) and \( \text{NWO} \), the number of W atoms in a tungstate cluster, however, is not found because of the strong contribution of local structural distortions in the tungstates.

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References and Notes


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