Structure and Electronic Properties of Solid Acids Based on Tungsten Oxide Nanostructures

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UV–visible diffuse reflectance spectroscopy was used to probe the electronic structure and domain size of tungsten oxide species in crystalline isopolytungstates, monoclinic WO₃, and dispersed WO₃ species on ZrO₂ surfaces. UV–visible absorption edge analysis, CO₂ chemisorption, and Raman spectroscopic results show that three distinct regions of WO₃ coverage on ZrO₂ supports appear with increasing WO₃ surface density: submonolayer region (0–4 W nm⁻²), polytungstate growth region (4–8 W nm⁻²), and polytungstate/crystalline WO₃ coexistence region (>8 W nm⁻²). The structure and catalytic activity of WO₃ species on ZrO₂ is controlled only by WO₃ surface density (W nm⁻²), irrespective of the WO₃ concentration, oxidation temperature, and ZrO₂ surface area used to obtain a particular density. The submonolayer region is characterized by distorted octahedral WO₃ species that are well dispersed on the ZrO₂ surface. These species show a constant absorption edge energy, they are difficult to reduce, and contain few acid sites where o-xylene isomerization can occur at 523 K. At intermediate WO₃ surface densities, the absorption edge energy decreases, WO₃ domain size increases, WO₃ species become easier to reduce, and o-xylene isomerization turnover rates (per W atom) increase with increasing WO₃ surface density. At high WO₃ surface densities, a polytungstate monolayer coexists with monoclinic WO₃ crystals. The growth of monoclinic WO₃ crystallites results in lower o-xylene isomerization turnover rates because WO₃ species become inaccessible to reactants. In the presence of H₂ at typical catalytic reaction temperatures (~523 K), strong acid sites form on WO₃–ZrO₂ catalysts with polytungstate domains by a slight reduction of the cluster and delocalization of an electron from an H atom resulting in H⁺₄ (Brønsted acid site).

1. Introduction

Strong solid acids based on supported transition-metal oxides are potential replacements for liquid acids and halide-containing solids.¹–² Acid site strengths and densities similar to those in sulfuric acid, halides, or oxyhalides remain elusive. Brønsted acid sites form on oxide-based solid acids when protons balance net negative charges introduced by substituting cations with a lower valence charge³ or by partial reduction of neutral oxide clusters.⁴ Sulfuric acid impregnated on zirconia supports has been extensively studied as a strong solid acid;⁵,⁶ their poor stability and their tendency to form volatile sulfur compounds even at low conversions.⁹ The addition of a small amount of H₂ at typical catalytic reaction temperatures (~523 K), strong acid sites form on WO₃–ZrO₂ catalysts with polytungstate domains by a slight reduction of the cluster and delocalization of an electron from an H atom resulting when hydrogen is present.⁴,¹⁰–¹³ On Pt/WO₃–ZrO₂ we have shown that efficient hydrogen transfer steps prevent extensive cracking of adsorbed carbenium ions by limiting their surface lifetimes.⁴ Several recent patents describe the synthesis and catalytic activity of WO₃–ZrO₂ and Pt/WO₃–ZrO₂ for several hydrocarbon reactions (cyclohexane ring-opening and isomerization, benzene hydrogenation, alkene oligomerization, aromatic alkylation with alkenes or methanol, aromatic trans-alkylation, and heteroatom removal).¹⁴

High turnover rates for acid-catalyzed isomerization on WO₃–ZrO₂ catalysts require the presence of WO₃ domains of intermediate size on ZrO₂ surfaces.³ Maximum o-xylene isomerization turnover rates occur at WO₃ surface densities (8–10 W nm⁻²)¹⁵ that exceed the theoretical monolayer capacity of ZrO₂ (7 W nm⁻²).¹⁶ o-Xylene isomerization turnover rates depend only on WO₃ surface density and not independently on WO₃ concentration, oxidation temperature, or ZrO₂ surface area. The presence of H₂ during o-xylene isomerization increases turnover rates and prevents rapid deactivation.¹⁵ X-ray absorption studies have shown that W centers reside in similar distorted octahedral environments for a wide range of WO₃ surface densities (3–15 W nm⁻²).¹³ WO₃ domains of intermediate size appear to provide a compromise between reducibility and accessibility of WO₃ centers. These WO₃ domains delocalize a net negative charge caused by the slight reduction of W⁶⁺ centers leading to the in situ formation of Brønsted acid centers (WO₃)ₙ⁻·{W⁶⁻ₙ₋₁O₃}{H⁺₄} in reactant environments containing H₂ or hydrocarbons.¹⁷
UV–visible diffuse reflectance spectroscopy is a useful spectroscopic technique that probes the electronic structure and domain size of transition-metal oxides. The position of the absorption edge is sensitive to the bonding between metal oxide polyhedra, and it has been used to characterize the average particle size of nano-crystalline insulators and semiconductors.

In our study, UV–visible absorption edge energies of WO$_3$ species on ZrO$_2$ supports are compared with the edge energies of several crystalline standards with known WO$_3$ coordination symmetry and domain size in order to determine how acid-catalyzed reaction rates depend on bonding between WO$_3$ species and WO$_3$ domain size. In addition, color changes associated with the reduction of these WO$_3$ domains in H$_2$ at ω-xylene reaction temperatures (523 K) are measured by the appearance of absorption bands at energies below the absorption edge. The rate of reduction of these neutral WO$_3$ domains may be related to the ability of these materials to form Brønsted acid sites under reaction conditions.

Raman spectroscopy is a valuable tool for the characterization of dispersed metal oxides. It detects vibrational modes of surface and bulk structures, which can be related to molecular structures by comparison with standard compound spectra or with theoretical calculations. The accuracy, reliability, and interpretation of the Raman spectra of metal oxide catalysts have been discussed recently. Supported tungsten oxide catalysts have been widely studied, with emphasis on samples with low WO$_3$ surface densities on γ-Al$_2$O$_3$ supports. Some recent studies of WO$_3$–ZrO$_2$ samples have detected polytungstate and crystalline WO$_3$ species at relative concentrations that depend on WO$_3$ concentration and oxidation temperature. In this study, Raman spectroscopy is used to determine how the intensity of bands corresponding to the internal W–O stretch in bulk WO$_3$ crystallites and the terminal W=O stretch are related to the dispersion of WO$_3$ species for dehydrated WO$_3$–ZrO$_2$ samples with a wide range of WO$_3$ concentrations (3–26 wt % WO$_3$) and oxidation temperatures (933–1283 K).

2. Experimental Section

2.1 Synthesis. ZrO$_2$(OH)$_{4−2x}$ supports (295 m$^2$ g$^{-1}$) were prepared by the hydrolysis of 0.5 M ZrOCl$_2$ (Aldrich Chemicals, >98%) aqueous solutions fed at 500 cm$^3$ h$^{-1}$ into a well-stirred vessel with a pH of 10 held constant by the controlled addition of NaOH (14 N). The precipitate was dried at 423 K overnight after residual Cl$^−$ ions were removed (<10 ppm) by thorough washing. The dry ZrO$_2$(OH)$_{4−2x}$ solids were impregnated to the point of incipient wetness with ammonium metatungstate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$, Strem Chemical, 99.9+%) aqueous solutions. These samples were placed in shallow quartz boats (5 g each), heated at 0.167 K s$^{-1}$ to the final oxidation temperature (773–1283 K), and held isothermal for 3 h in dry air flowing through a 25 mm quartz tube (4 cm$^3$ s$^{-1}$). Tungsten oxide loadings are reported as a percent by weight of WO$_3$ (0–26 wt % WO$_3$) in the oxidized (dehydrated) samples. Several samples were analyzed by atomic absorption to confirm the accuracy of these nominal WO$_3$ loadings (± 0.3 wt % WO$_3$) and to show that WO$_3$ does not sublime even at the highest oxidation temperatures of our study.

2.2 UV–Visible Diffuse Reflectance Spectroscopy. Ultraviolet–visible (UV–vis) diffuse reflectance spectra of WO$_3$–ZrO$_2$ samples and standard WO$_3$ compounds were obtained using a Varian (Cary 4) spectrophotometer with a Harrick-Scientific Praying-Mantis diffuse reflectance accessory and in situ cell (DRA-2CR). Samples were lightly ground using an agate mortar and pestle to form agglomerates smaller than 0.1 mm and dehydrated in the reflectance accessory at 723 K for 2 h in flowing dry air (Matheson, Ultra Zero Grade, 2.0 cm$^3$ s$^{-1}$) purified with a 13X molecular sieve in order to remove residual water and hydrocarbons. The Kubelka–Munk function ($F(R_a)$, eq 2) for infinitely thick samples was used to convert reflectance measurements ($R_{sample}$) into equivalent absorption spectra$^{25}$ using the reflectance of MgO as a reference ($R_{MgO}$).

$$R_a = \frac{R_{sample}}{R_{MgO}}$$

$$F(R_a) = \frac{(1 - R_a)^2}{2R_a} = \alpha (\text{absorption coefficient}) \frac{S(\text{scattering coefficient})}{R}$$

2.3 Chemisorption Studies. Chemisorption data were collected using a Quantachrome 1C Autosorb apparatus. Samples were heated in He at 0.083 K s$^{-1}$ to 673 K and held for 4 h in order to remove adsorbed H$_2$O and CO$_2$ before CO$_2$ adsorption measurements. After cooling to 313 K, samples were evacuated and a CO$_2$ adsorption isotherm was obtained between 2.7 and 53 kPa. The low-pressure linear part of the isotherm was extrapolated to zero pressure to calculate chemisorption uptakes. Samples for H$_2$ chemisorption were dried at 723 K in air and reduced in H$_2$ at 523 K for 1 h. After evacuation, H$_2$ adsorption isotherms were obtained between 2.7 and 53 kPa H$_2$ at 523 K. Physical surface areas were obtained by N$_2$ physisorption at 77 K (after dehydration in N$_2$ for 2 h at 473 K) using a Quantasorb surface area analyzer (Quantachrome Corporation) and standard multi-point BET methods.

2.4 Raman Spectroscopy. Raman spectra were obtained using a HoloLab 5000 Research Raman Spectrometer (Kaiser Optical Systems, Inc.) equipped with a 532 nm diode-pumped solid-state laser (Coherent Laser Group) and a thermoelectrically cooled CCD detector (Princeton Instruments, Inc.). WO$_3$–ZrO$_2$ samples were pressed into 1.0 cm diameter wafers and placed within a controlled atmosphere quartz cell containing Heraeus Amsris Suprasil 311 quartz optical windows. Samples were dehydrated in situ by heating to 673 K in flowing air (Zero Grade, 1 cm$^3$ s$^{-1}$) for 1 h and then cooled to 373 K to measure Raman spectra. Spectra were normalized by the applied laser power (laser exposure time). Mixtures of Lorentzian and Gaussian basis functions were chosen to fit Raman spectra using nonlinear least-squares methods.

3. Results/Discussion

3.1 Analysis of UV–Visible Absorption Edge Energy. The optical absorption edge energies of crystalline and amorphous WO$_3$ species were obtained from diffuse reflectance UV–vis absorption spectra. The optical absorption edge energy is defined as the minimum photon energy required to excite an electron from the highest occupied molecular orbital (HOMO, at the top of the valence band in semiconductor domains) to the lowest unoccupied molecular orbital (LUMO, at the bottom of the conduction band). There are two basic types of electronic transitions, direct and indirect.$^{26}$ Direct transitions require only that photons excite electrons, while indirect transitions also require concerted vibrations and energy from the crystal lattice (phonons). The energy dependence of the absorption coefficient ($\alpha$) for semiconductors in the region near the absorption edge is given by

$$\alpha \propto \frac{(h \nu - E_0)^n}{h \nu}$$

Where $h \nu$ is the photon energy, $E_0$ is the energy of the conduction band minimum, and $n$ is the bandgap transparency index. In our study, $n$ was determined by nonlinear least-squares methods.
where $h\nu$ is the energy of the incident photon and $E_o$ is the optical absorption edge energy; the exponent $\eta$ depends on the type of optical transition caused by photon absorption.\textsuperscript{26} In crystalline semiconductors, where crystal momentum is conserved and electron transitions obey well-defined selection rules, $\eta$ is 1/2, 3/2, 2, and 3 when the transitions are direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden, respectively. In general, transitions that are forbidden by symmetry selection rules have a lower probability of occurring [$P_{\eta} \propto (h\nu - E_o)^{3/2}$] and transitions that require phonons have an additional $(h\nu - E_o)^{1/2}$ factor that arises from the dependence of the absorption coefficient on phonon energy. In amorphous, homogeneous semiconductors, the value of $\eta$ is 2 irrespective of the type of transition found in crystalline materials of the same composition.\textsuperscript{27} The momentum vector is not conserved in amorphous materials; therefore, an integration has to be performed over the density of states, resulting in an energy dependence similar to that for indirect transitions.

With an appropriate choice of $\eta$, a plot of $(\alpha h\nu)^{1/\eta}$ vs $h\nu$ is linear near the edge and the intercept of the line on the abscissa $(\alpha h\nu)^{1/\eta} = 0$ gives the optical absorption edge energy $E_o$. Previous studies have shown that the fundamental absorption edge of WO\textsubscript{3} crystallites is caused by indirect electron transitions\textsuperscript{28} and that a plot of $(\alpha h\nu)^{1/\eta}$ vs $h\nu$ is linear near the edge for amorphous WO\textsubscript{3} films.\textsuperscript{29} We find a similar linear dependence for small WO\textsubscript{3} domains, for which band theory does not strictly apply. A large density of available 5d states and static disorder in W=O bond lengths and angles leads to a broad distribution of states that can be analyzed using methods applicable to bands of energy levels. Therefore, a value of $\eta = 2$ was used in this study in order to define the absorption edge for WO\textsubscript{3}−ZrO\textsubscript{2} samples containing crystalline WO\textsubscript{3} or amorphous WO\textsubscript{3} species in isolated or polytungstate domains.

In the diffuse reflectance experiments, UV−vis reflectance data cannot be used directly to measure absorption coefficients ($\alpha$) because of scattering contributions to the reflectance spectra. Scattering coefficients, however, depend weakly on energy and $F(R_o)$ can be assumed to be proportional to the absorption coefficient within the narrow range of energy containing the absorption edge features. Then, a plot of $(F(R_o) h\nu)^{1/\eta}$ vs $h\nu$ can be used to determine the absorption edge energy. An excellent fit was obtained using this method ($\eta = 2$) for amorphous WO\textsubscript{3} domains on ZrO\textsubscript{2} and for a crystalline monoclinic WO\textsubscript{3} sample (Figure 1), which confirms that this method gives a precise value of the absorption edge energy ($\pm0.03$ eV). Most absorption spectra in this study, including those of molecular WO\textsubscript{3} clusters, are also described accurately in this manner as determined by the linearity of the plot when $\eta = 2$. WO\textsubscript{3}−ZrO\textsubscript{2} samples containing two or more distinct WO\textsubscript{3} structures, however, require deconvolution to separate the multiple absorption edges. The nonlinear region found at energies lower than $E_o$ is known as the Urbach tail,\textsuperscript{30} it is related to low-frequency acoustic modes that lead to fluctuations in the band gap. It is often represented by an empirical relation valid for $h\nu < E_o$:

$$\alpha \propto \exp\{\rho(h\nu - E_o)/kT\}$$  \hspace{1cm} (4) 

where $\sigma$ is a constant.

It is interesting to note that the other crystalline d\textsuperscript{0} transition metal oxides (MoO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, and TiO\textsubscript{2}) also show an indirect absorption edge and can be analyzed by the method outlined above (with $\eta = 2$).\textsuperscript{31} Several studies, however, have described UV−vis spectra using the formalism for direct-allowed transitions ($\eta = 1/2$)\textsuperscript{18,32} or the position of the first absorption maximum.\textsuperscript{33,34} Methods based on direct transitions or peak position emphasize the region of high optical absorption near the edge, where the Kubelka−Munk function becomes nonlinear in absorber concentration and underlying assumptions become inaccurate.\textsuperscript{35}

3.2 UV−Visible Absorption Spectra of Tungsten Oxide Standards. UV−vis absorption spectra were measured for various crystalline WO\textsubscript{3} standard compounds of known composition and structure. These samples cover a wide range of WO\textsubscript{3} domain size, coordination symmetry, and absorption edge energy (Figure 2). Dehydrated Na\textsubscript{2}WO\textsubscript{4}·H\textsubscript{2}O (Aldrich Chemicals, 99.995%) consists of molecular (isolated) four-coordinate W\textsuperscript{6+} centers tetrahedrally coordinated to oxygens\textsuperscript{36} and gave the highest absorption edge energy value (4.89 eV) among the
samples examined. Six-coordinate W⁶⁺ in monoclinic WO₃ (Aldrich Chemicals, 99.995%), which contains WO₃⁻ species in an extended three-dimensional crystalline network of distorted octahedra bonded to six neighboring octahedra (distorted ReO₃ structure), gave the lowest absorption edge energies (2.59 eV). WO₃ domains of intermediate size, such as those found in isotropic tungstate clusters containing octahedra bonded through corners and edges, showed intermediate values of the absorption edge energies. For example, absorption edge energies for W₁₂ clusters in ammonium metatungstate [(NH₄)₆H₂W₁₂O₄₀, Strem Chemicals, 99.9%] and ammonium paratungstate [(NH₄)₆H₂W₁₂O₄₂, K&K Laboratories 99.9%] were 3.23 and 3.54 eV, respectively.

The absorption edge energy for these crystalline WO₃ standards is strongly influenced by the number of WO₃ polyhedra neighbors bonded through W—O—W bonds and by the number of bonds between each polyhedra. Quasi-infinite WO₃ domains in monoclinic WO₃ contain WO₆ octahedra with six WO₆ neighbors and have an edge energy that is 2.3 eV lower than that found for isolated WO₃ species. The smaller difference in the absorption edge energies between the two polytungstate clusters, both of which contain WO₆ octahedra with four WO₆ neighbors, reflects differences in bonding between the WO₆ octahedra. Metatungstate contains a larger fraction of edge-sharing octahedra relative to corner-sharing octahedra and therefore has greater molecular orbital overlap between octahedra and a narrower HOMO—LUMO gap because of the more extensive “communication” of electrons between octahedra.

Weber reported an apparent linear correlation between the number of nearest MoO₆ neighbors in crystalline MoO₃ standards and the absorption edge energy calculated using the formalism for direct-allowed electronic transitions (η = 1/2). Detailed analysis, however, suggests that the fundamental absorption edge for crystalline MoO₃ arises from indirect-allowed electronic transitions, although analysis based on direct transitions leads to similar qualitative trends with domain size. This analysis based solely on the number of nearest neighbors provides a useful directional relationship, but it neglects smaller shifts in the absorption edge energy as a result of differences in bonding configuration (edge- or corner-shared polyhedra) and of bonding between the polyhedra and the support. In this manner, the number of nearest neighbors in amorphous samples may be approximated using the absorption edge energy of crystalline standards if the details in bonding between polyhedra and support effects are also considered.

The absorption edge energy has also been shown to depend on crystallite size for small semiconductor nanocrystals (<100 nm) for which bonding geometry remains the same. The energy of an electronic transition is well defined for any crystallite size. The momentum of the excited electron, however, becomes less accurately defined as the position is restricted by placing it within smaller crystallites. As a result, the separation among energy levels or bands increases as the crystallite size is reduced, as in the “particle-in-a-box” construct of elementary quantum mechanics. These quantum confinement effects have been described accurately by an analytical expression (eq 5) that can be used to calculate experimental shifts of absorption energies (ΔE) with crystallite size for crystallites larger than 2 nm.

\[ \Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{eR} + \text{polarization term} \]  

This expression becomes inaccurate for domains smaller than 2 nm, because the periodic lattice and effective mass approximations required in its derivation become inappropriate. For these small domains (<2 nm), extended Hückel calculations have been used to predict the separation between energy levels. Calculations for MoO₃ clusters have confirmed that the separation between energy levels continues to increase for crystalline domains smaller than 2 nm. These calculations have also confirmed that the HOMO—LUMO gap strongly depends on the number of nearest polyhedral neighbors and the number of bonds between each of those neighbors (corner- or edge-shared polyhedra). In addition, these studies have shown that absorption energies are influenced less by the local symmetry around Mo⁶⁺ centers (tetrahedral or octahedral) and by the metal—oxygen bond lengths.

3.3 UV—Visible Absorption Spectra of WO₃—ZrO₂ Samples. UV—vis diffuse reflectance absorption spectra of WO₃—ZrO₂ with varying WO₃ concentrations and oxidation temperatures are shown in Figures 3–5. A sharp rise in absorption occurs between 2.6 and 3.6 eV as a result of ligand-to-metal charge transfer (O₂p → W⁵d—O₂p); the energy required for this transition depends strongly on WO₃ concentration and oxidation temperature. UV—vis absorption spectra for a 26% WO₃—ZrO₂ sample oxidized at temperatures between 773 and 1073 K are shown in Figure 3. The absorption spectra shift to lower energies with increasing oxidation temperature and a second edge appears, at an energy similar to that in bulk monoclinic WO₃ crystals, when oxidation is carried out above 1073 K. On the latter samples, the presence of crystalline WO₃ has been confirmed by X-ray diffraction. Increasing oxidation temperature leads to increased ZrO₂ sintering rates and loss of support surface area. As a result, the average distance between dispersed WO₃ octahedra on the ZrO₂ surface decreases and WO₃ surface density increases with increasing oxidation temperature. As the coverage of ZrO₂ support by WO₃ species increases, the dispersed WO₃ species eventually form W—O—W bridging bonds between neighboring WO₃ groups, resulting in the formation of two-dimensional polytungstates and three-dimensional WO₃ crystallites. The formation of these W—O—W bonds between WO₃ octahedra leads to larger domains and to a narrowing of the HOMO—LUMO gap, as predicted by Masure et al. and confirmed by the data in Figure 3.
Absorption spectra for several WO$_x$–ZrO$_2$ samples containing 3–26 wt % WO$_3$ oxidized at 973 K or at 1073 K are compared in Figures 4 and 5 with spectra for ZrO$_2$ (oxidized at 873 K). The absorption spectra for various crystalline ZrO$_2$ samples (not shown) are nearly independent of crystallite size and type (monoclinic or tetragonal); therefore, only a single ZrO$_2$ spectrum is included as reference. Clearly, a second absorption edge corresponding to ZrO$_2$ appears in all WO$_x$–ZrO$_2$ samples with WO$_x$ concentrations less than 20 % WO$_3$. The intensity of the WO$_x$ absorption edge increases and shifts to lower energies with increasing WO$_x$ concentration as expected from the growth of WO$_x$ domains by formation of corner- and edge-shared WO$_x$ octahedra at higher WO$_x$ surface densities. This increase in WO$_x$ concentration has an effect similar to that of increasing the oxidation temperature, because they both tend to increase the WO$_x$ surface density and domain size.

3.4 UV–Visible Optical Absorption Edge Energies. 3.4.1 WO$_x$ Surface Density and Domain Size. Optical absorption edge energies were calculated from UV–vis diffuse reflectance spectra for the WO$_x$–ZrO$_2$ samples from Figures 3–5 and several other WO$_x$–ZrO$_2$ samples at other WO$_x$ concentrations and oxidation temperatures using the formalism for indirect transitions given by eq 3 ($\eta = 2$). Absorption edge energies fall into a single curve for all samples when plotted against WO$_x$ surface density (W nm$^{-2}$, from BET surface area measurements and WO$_x$ concentration), irrespective of whether WO$_x$ surface density changed because of varying WO$_x$ concentration or oxidation temperature (Figure 6). Therefore, the electronic structure and the domain size of WO$_x$ species on ZrO$_2$ surfaces depend only on WO$_x$ surface density. In a previous study, we have also shown that the rate of o-xylene isomerization (per W atom) on these samples also depends only on WO$_x$ surface density, and not the method used to achieve it. The dashed “volcano curve” in Figure 6 shows the previously reported dependence of isomerization rate on WO$_x$ surface density for comparison.

The data in Figure 6 suggest that absorption edge energies can be grouped into three distinct regions with characteristic surface density ranges of 0–4 W nm$^{-2}$, 4–8 W nm$^{-2}$, and >8 W nm$^{-2}$. Within the first region, the absorption edge energy is 3.49 ± 0.02 eV and it is not affected by WO$_x$ surface density. In the second region, the absorption edge shifts linearly from 3.49 to 3.16 eV, and it maintains a constant value of 3.16 ± 0.05 eV above 8 W nm$^{-2}$ in the third region. In this latter region, a second absorption edge appears at 2.6 eV, the absorption intensity of which increases monotonically with increasing WO$_x$ surface density.

The density of acid sites (per W atom) detected by acid-catalyzed isomerization reactions reaches a maximum (reflected in the isomerization rate per W atom) at WO$_x$ densities of about 8–9 W nm$^{-2}$ (dashed curve in Figure 6). The data in this volcano-shaped curve also contain three distinct regions that can be grouped within ranges of WO$_x$ surface densities (0–4, 4–9, and >9 W nm$^{-2}$) similar to those used for UV–visible edge energies. At low WO$_x$ surface densities (<4 W nm$^{-2}$),

![Figure 4](image1.png)

**Figure 4.** Diffuse reflectance UV–vis absorption spectra of WO$_x$–ZrO$_2$ samples oxidized at 973 K containing (A) 26%, (B) 20%, (C) 12%, (D) 9%, (E) 3%, and (F) 0% WO$_3$.

![Figure 5](image2.png)

**Figure 5.** Diffuse reflectance UV–vis absorption spectra of WO$_x$–ZrO$_2$ samples oxidized at 1073 K containing (A) 26%, (B) 15%, (C) 12%, (D) 9%, (E) 3%, and (F) 0% WO$_3$.

![Figure 6](image3.png)

**Figure 6.** Indirect absorption edge energies of WO$_x$–ZrO$_2$ samples at several oxidation temperatures and tungsten loadings. Two crystalline tungsten oxide materials (monoclinic WO$_3$ and ammonium metatungstate) are shown for reference. Dashed curve is a summary of o-xylene isomerization rates per W atom, 15$^{[523 K, 0.66 kPa o-xylene, 100 kPa H_2]}$.
reaction rates are too low to measure. Isomerization rates increase with increasing WO₆ density for values between 4 and 9 W nm⁻², and then decrease for densities higher than 9 W nm⁻². Near-edge X-ray absorption spectra of dehydrated WOₓ-ZrO₂ with a wide range of WO₆ surface density (3–15 W nm⁻²) has shown that W₆⁺ centers are present in distorted octahedra similar to each other and similar to those in crystalline WO₃ throughout the entire range of WO₆ surface density. Thus, the observed changes in o-xylene isomerization rates cannot be attributed to the evolution of less-active tetrahedral WO₄ into more active W species with octahedral structure as WO₆ surface density increases, a process detected for WO₆ species on WOₓ-Al₂O₃ samples. At low WO₆ surface densities, tetrahedral WO₄ species form on Al₂O₃ because stable Al₂(WO₄)₃-like species can form, whereas there are no tetrahedral WO₆ species found on ZrO₂, because none of the known Zr(WO₄)₂ structures exhibit tetrahedral WO₄ centers.

3.4.2 Low WO₆ Surface Densities. WOₓ–ZrO₂ samples with low WO₄ surface densities (0–4 W nm⁻²) show a constant absorption edge energy (3.49 eV) and contain very few acid sites capable of o-xylene isomerization at 523 K. The constant absorption edge energy suggests that the connectivity between WO₆ groups is not influenced by surface density at low submonolayer coverages. Extended Hückel calculations predict that the formation of metal oxide dimers and oligomers from isolated oxide species would shift absorption edge energies to lower values. Apparently, WO₆ groups do not interact with each other to form bridging W–O–W bonds until surface densities are greater than 4 W nm⁻². Below 4 W nm⁻², the ZrO₂ surface stabilizes dispersed WO₆ species that are electronically isolated from each other (Scheme 1a). Near-edge X-ray absorption spectra show that these isolated WO₆ species exist in distorted octahedral symmetry, and temperature-programmed reduction studies indicate that these species reduce in H₂ at significantly higher temperatures than polytungstate species or WO₆ crystallites. The absorption edge energy for these dispersed WO₆ octahedra on ZrO₂ (3.49 eV) is significantly lower than the edge energy for truly isolated WO₄ tetrahedra in Na₂W₂O₇ (4.89 eV), and resemble more closely the dispersed WO₄ tetrahedra present on Al₂O₃ (3.95 eV). It is likely that the large distortions to the WO₆ polyhedra caused by covalent bonds with ZrO₂ or Al₂O₃ increase the effective domain size of the dispersed WO₆ polyhedra by allowing the delocalization of electrons within the Zr or Al next nearest neighbors, but to a lesser extent than when the next nearest neighbor is W.

Carbon dioxide chemisorption uptakes were used to measure the fraction of the ZrO₂ support covered by WO₆ species. Carbon dioxide selectively binds to basic sites on ZrO₂ and therefore was used to determine the fraction of exposed ZrO₂. This method has been shown to accurately determine the coverage of TiO₂ supports by WO₆ species. The average value of CO₂ chemisorption uptakes at 313 K on several pure ZrO₂ samples oxidized at various temperatures (773–1073 K) was used to determine the fraction of the ZrO₂ surface covered by WO₆. Carbon dioxide chemisorption uptakes on bulk WO₃ crystallites were negligible (0.01 CO₂-molecules nm⁻²). The calculated WO₆ coverage on ZrO₂ increases linearly as WO₆ surface density increases within the submonolayer region (0–4 W nm⁻²). WO₆ coversages reach a constant value of about 90% at 4.0 W nm⁻² and do not increase further as WO₆ surface density increases, suggesting that a small fraction of basic sites on ZrO₂ remains exposed even at WO₆ densities for which the condensation of WO₆ octahedra and formation of three-dimensional clusters occurs.

The linear increase in coverage with increasing WO₆ surface density between 0 and 4 W nm⁻² is consistent with well-dispersed WO₆ species (Scheme 1a) that titrate CO₂ binding sites on ZrO₂ with 1:1 stoichiometry. Apparently, these isolated WO₆ species are stabilized through multiple W–O–Zr bonds between each WO₆ octahedra and the ZrO₂ surface. These isolated WO₆ octahedra reach saturation coverage (4 W nm⁻²) at about half of the theoretical polytungstate monolayer (7.8 W nm⁻²), which was estimated by the density of WO₆ species in a two-dimensional plane of corner-shared WO₆ octahedra with W–O bond distances corresponding to those in low-index planes of monoclinic WO₃ crystallites. This saturation coverage of isolated monomutagstate species on ZrO₂ agrees well with previous estimates from Raman spectroscopic data (4.0 W nm⁻²). At WO₆ surface densities within the submonolayer region (0–4 W nm⁻²), optical absorption spectra, CO₂ chemisorption uptakes, and X-ray absorption spectra are all consistent with the existence of isolated monomutagstate WO₆ octahedra that are difficult to reduce and are not able to promote the isomerization of o-xylene at 523 K.

3.4.3 Intermediate WO₆ Surface Densities. At intermediate WO₆ surface densities (4–8 W nm⁻²), absorption edge energies decrease and o-xylene isomerization rates per W atom increase markedly as WO₆ surface density increases. The decrease in edge energy shows that electrons become delocalized in larger domains through bridging W–O–W bonds that are found within polytungstate two-dimensional structures (Scheme 1b) and small (WO₆)ₙ clusters. Initial W–O–W bonds form by condensation of isolated WO₆ species as the surface area of the ZrO₂ support decreases and the WO₆ surface density increases during oxidation treatments. Increasing the surface density of WO₆ species within this region (4–8 W nm⁻²) leads to a monotonic increase in WO₆ domain size until a constant domain size is reached corresponding to a polytungstate monolayer at about 8 W nm⁻². The density of WO₆ species within this polytungstate monolayer is very similar to the theoretical polytungstate monolayer (7.8 W nm⁻²).

The edge energies of these two-dimensional polytungstate structures (3.16–3.49 eV) are very similar to those in isopolytungstates (e.g., ammonium metatungstate, (NH₄)₆H₂W₁₈O₆₄(₂), 3.25 eV) (Figure 6). Temperature-programmed reduction studies of WO₆–ZrO₂ samples with intermediate WO₆ surface densities
show that these polytungstate species begin to reduce at temperatures that are quite similar to a heteropolytungstate (12-tungstophosphoric acid) and at significantly lower temperatures than isolated WO$_x$ species.\textsuperscript{17} WO$_x$ octahedra in these three-dimensional heteropolytungstates are connected within the wrapped surface and not through the center insulating atom; therefore, their domain size and reducibility is close to that of a two-dimensional polytungstate. Maximum o-xylene isomerization rates and therefore highest acid site densities are also found on WO$_x$-ZrO$_2$ catalysts near polytungstate saturation coverages because of an apparent compromise between WO$_x$ accessibility to reactants and the ease of reduction of WO$_x$ domains; the latter appears to be required in order to form Bronsted acid sites from neutral WO$_x$ species\textsuperscript{17} (Scheme 2). Hydrogen chemisorption and reduction measurements confirming this proposal are reported as a function of WO$_x$ surface density in the last section of this paper. These measurements provide strong evidence for Bronsted acid site generation via the mechanism in Scheme 2.

3.4.4 High WO$_x$ Surface Densities. At high WO$_x$ surface densities (>8 W nm$^{-2}$), absorption edge energies remain constant at 3.19 eV and a second absorption edge appears at lower energies (2.61 eV) for surface densities above 12 W nm$^{-2}$ (Figure 6). The intensity of this new absorption feature increases with increasing WO$_x$ surface density and occurs at an energy similar to that in monoclinic WO$_3$ crystallites. X-ray diffraction detects the incipient formation of WO$_3$ crystallites at surface densities above 10 W nm$^{-2}$.\textsuperscript{14} WO$_3$ crystallites on the latter WO$_x$-ZrO$_2$ samples are also apparent from their yellow color, their Raman spectra (Figure 8), and from the appearance of a distinct WO$_3$ to WO$_3$ reduction feature in temperature-programmed reduction profiles.\textsuperscript{17} We have previously suggested that the decrease in o-xylene isomerization rates per W atom observed in these samples with increasing surface density is caused, in part, by a decrease in WO$_3$ dispersion, which leads to inaccessible WO$_x$ species within WO$_3$ crystallites.\textsuperscript{17}

The absorption edge energy for polytungstate structures in samples containing WO$_3$-like absorption features is difficult to extract from experimental spectra because of significant overlap between WO$_3$ and polytungstate features. For these samples, a scaled spectrum for bulk WO$_3$ was subtracted from WO$_x$-ZrO$_2$ spectra in order to resolve the polytungstate absorption edge. Nonlinearities in the Kubelka–Munk function at high absorber concentrations resulted in imperfect fits when these pseudo-absorption spectra were used to describe the spectra for physical mixtures of pure crystalline WO$_3$ and ZrO$_2$. The absolute error in edge energies for these mixtures, however, was only ±0.1 eV, and the method was used to obtain the edge energy values for samples with surface densities above 12 W nm$^{-2}$ (Figure 6). These extracted edge energies are very similar to those measured for polytungstate species that lead to maximum o-xylene isomerization rates. This bimodal distribution of edge energies suggests that polytungstate monolayers on ZrO$_2$ are very stable and that WO$_x$ species in excess of those required to form this monolayer bind weakly to it and tend to agglomerate into WO$_3$ crystallites during oxidation [Scheme 1c]. The stability of polytungstate monolayers on ZrO$_2$ is related to the strong W–O–Zr bonds between the WO$_x$ octahedra and the ZrO$_2$ surface as suggested by high reduction temperatures of isolated WO$_x$ species and by their stabilization of ZrO$_2$ surface area.\textsuperscript{4} Crystallites of bulk WO$_3$ grow from the excess WO$_x$ species because the W–O–W bonds that bind these octahedra to the polytungstate layer are weaker than the W–O–Zr bonds, and
at the high oxidation temperatures used these octahedra can migrate on the surface and agglomerate into crystals of WO₃ that minimize surface free energy.

An attempt to quantify the amount of crystalline WO₃ in WOₓ−ZrO₂ samples based on the WO₃ absorption spectrum scaling factor gave inaccurate results. Samples containing similar amounts of bulk WO₃ but with different crystallite sizes resulted in a WO₃ scaling factor that varied with crystallite size. The penetration depth of photons in WO₃ species is expected to be quite small at energies above the absorption edge energy; therefore, only a small fraction of the WO₃ absorbers in a large WO₃ crystallite are probed by incoming photons. As a result, large WO₃ crystallites that consist primarily of internal WO₃ species have a much smaller effective absorption cross sections than smaller WO₃ crystallites, making calculations of the amount of crystalline WO₃ from UV–vis absorption measurements inaccurate.

3.5 Raman Spectra of WOₓ−ZrO₂ Samples. Raman spectra of several dehydrated WOₓ−ZrO₂ samples and of crystalline WO₃ are shown in Figure 8. Polytungstate structures, with a Raman band at 880 cm⁻¹,²² are observed in the WOₓ−ZrO₂ sample with the lowest WO₃ surface density (4.5 W nm⁻², Figure 8(E)). The strong Raman feature at 1019 cm⁻¹ in this sample has been assigned to the symmetric stretch mode of terminal W=O bonds,⁴³ which are present in monotungstate and polytungstate species and at the surface of WO₃ crystals. WO₃ species also show Raman bands below 680 cm⁻¹, but these features overlap with those of tetragonal and monoclinic ZrO₂. The incipient formation of crystalline WO₃ appears at WO₃ surface densities above 4.5 W nm⁻². Raman bands corresponding to crystalline WO₃ (Figure 8(A)) appear at 808, 720, and 275 cm⁻¹; these bands correspond to W=O stretching, W=O bending, and W=O=W deformation modes, respectively.⁴⁵,⁴⁶ Raman scattering cross sections for crystalline WO₃ are much greater than for surface polytungstate species;⁴⁷ as a result, WO₃ bands tend to dominate the spectra and prevent the detection of polytungstate species, even when the latter are the most abundant surface structures. At intermediate WO₃ surface densities (5–9 W nm⁻²), the small WO₃ crystals detected by Raman are below the detection limit of X-ray diffraction and UV–vis absorption measurements. Their detection in Raman spectra suggest that the same mechanism that leads to polytungstate species occasionally leads to a very small fraction of weakly bound WO₃ species that agglomerate into small WO₃ crystals. As WO₃ surface density increases further, the bands at 807, 720, and 270 cm⁻¹ become more intense, while the intensity of the 1019 cm⁻¹ band remains almost constant.

In spectrum B (Figure 8(B); 6% WO₃, 1223 K oxidation, 11.2 W nm⁻²), W=O bands for WO₃ clusters (270, 720, and 807 cm⁻¹) and terminal W=O bands (1019 cm⁻¹) are similar in intensity to those of samples with similar surface density (spectrum D; 15% WO₃, 1123 K oxidation, 10.8 W nm⁻²) but with different WO₃ concentration and oxidation temperature. These data confirm that WO₃ structures depend only on WO₃ surface density and not on WO₃ concentration or oxidation temperature independently, a conclusion reached from the UV–vis data in the previous section.

The ratio of integrated peak areas of the W=O stretch (807 cm⁻¹) in microcrystalline WO₃ and the symmetric stretch of terminal (surface) W=O (1019 cm⁻¹) is shown in Figure 9 for dehydrated WOₓ−ZrO₂ samples with various WO₃ surface densities (3–28 W nm⁻²). The intensity ratio increases from a value of zero for monotungstate species lacking W=O=W bonds (<5 W nm⁻²) to very large values as the spectrum of large WO₃ crystallites becomes dominated by bulk W=O=W features. As WO₃ surface density increases, the relative number of W=O bonds within microcrystalline WO₃ and polytungstate structures increases as WO₃ domains grow in size, while the number of surface (terminal) W=O remains almost constant. The observed increase in the ratio of intensities for these two bands shows that the concentration of WO₃ species in WO₃ clusters increases as WO₃ density increases. This is consistent with the UV–vis absorption edge results at >8 W nm⁻², which suggest that upon formation of a stable polytungstate monolayer on ZrO₂ excess weakly bound WO₃ species readily agglomerate into WO₃ crystallites. The accessibility of WO₃ species to reactants and their catalytic effectiveness decrease as WO₃ clusters grow with increasing surface density.

3.6 Reduction of WO₃ Species and the Formation of Brønsted Acid Sites and Color Centers in H₂. We have shown that o-xylene isomerization rates and acid site densities for WO₃ species on ZrO₂ supports reach a maximum value at intermediate WO₃ surface densities, for which a large fraction of the WO₃ species reside on the surface of polytungstate clusters and Brønsted acid sites form by delocalization of an electron from an H atom resulting in H₄⁺ species.¹⁵ H₂ has a promoting effect on the rate of acid catalysis on WO₃−ZrO₂, and appears to be required for the formation on Brønsted acid sites in neutral WO₃ structures.¹⁵

WOₓ−ZrO₂ samples with >4 W nm⁻² acquire absorption bands in the visible region of the spectra in the presence of H₂ at a typical reaction temperatures (523 K). The appearance of absorption bands in the visible region can be visually detected by a change in color from white or light yellow to blue. In a similar manner, crystalline WO₃, yellow in color, forms a blue hydrogen bronze (H₄WO₁₃) in the presence of H₂ at 523 K, Figure 10. These color centers form in WOₓ−ZrO₂ samples without any changes in the absorption edge energy, suggesting that their formation does not reflect changes in WO₃ domain size, but instead changes caused by placement of H atoms at the surface and in the bulk of WO₃ domains. Absorption of visible light at energies lower than the absorption edge occurs because electrons from the H atoms are inserted into the WO₃...
LUMO and can be optically excited into unoccupied states available at slightly higher energies. Similar processes appear to account for the appearance of Brønsted acidity; they require the presence of H₂ at temperatures sufficient for its dissociation and WO₃ structures capable of stabilizing the resulting H atoms as H⁺ by the mechanism in Scheme 2.

The rate of formation of these color centers, which is related to the relative ability of the WO₃ clusters to accommodate an H atom with its corresponding electron, was measured for several WO₃-ZrO₂ samples (26 wt % WO₃, 773–1073 K oxidation) with a wide range of WO₃ surface densities (4–16 W nm⁻²), Figure 11. Initial rates of formation were determined by integration of the Kubelka–Munk function (F(Rₜₒ)) across the broad absorption band that appears during exposure to H₂ at 523 K in the visible region (1.8–2.2 eV). The rate of formation of color centers is very low for the WO₃-ZrO₂ sample with the lowest WO₃ surface density (4.1 W nm⁻²). These rates increase with increasing WO₃ surface density, and they approach those measured on bulk WO₃ crystallites. This suggests that dispersed WO₃ species cannot accommodate the negative charge required to stabilize H⁺, whereas polytungstate and crystalline WO₃ structures stabilize H⁺ with greater ease as WO₃ domain size increases. The H atoms are stabilized by donation of an electron to electronegative WO₃ domains (polytungstate or WO₃ clusters), which delocalize the negative charge with increasing effectiveness as the size of these WO₃ domains increases. Apparently, as absorption edge energies decrease, WO₃ domains accept electrons with greater ease because electrons are placed in unoccupied molecular orbitals available at lower energies. Effective WO₃-ZrO₂ solid acids require that WO₃ domains must be large enough to stabilize negative charge and charge-compensating H⁺ species, but small enough to ensure that a large fraction of the WO₃/H⁺ remains accessible to reactants.

Hydrogen chemisorption uptakes were measured for several of these samples in order to determine the number of H atoms that reversibly bind to the WO₃ species at typical o-xylene isomerization reaction temperatures (523 K) after hydrogen pretreatment and evacuation at the same temperature, Table 1. Maximum hydrogen uptakes were recorded on the WO₃-ZrO₂ sample showing maximum isomerization rates (0.026 H/W, 8.5 W nm⁻²), suggesting that the formation of these reduced centers is indeed related to the stabilization of carboxatonic intermediates. When the o-xylene isomerization rate on this WO₃-ZrO₂ sample is normalized to the hydrogen uptake the apparent Brønsted acid site turnover rate (8.1 × 10⁻² (H atom)⁻¹ s⁻¹) is much higher than that reported for zeolites (H⁺-ZSM5, Si/Al = 14.5, 0.17 × 10⁻² (Al atom)⁻¹ s⁻¹) under similar reaction conditions (0.66 kPa o-xylene, 100 kPa H₂, 523 K).

Hydrogen uptakes were very low on WO₃-ZrO₂ samples with low WO₃ surface densities (0.001 H/W, 4.1 W nm⁻²), because the isolated WO₃ species are unable to delocalize the negative charge required to stabilize high H⁺ concentrations. Extended WO₃ domains that form at higher WO₃ surface densities can delocalize the negative charge throughout several WO₃ neighbors. This mechanism of delocalization of charge among several WO₃ groups and formation of Brønsted acid centers is similar to the generation of the strong acid sites on heteropolytungstate clusters, where the negative charge on the central anion is delocalized over the WO₃ shell and balanced by H atoms with a net positive charge (e.g., 12-tungstophosphoric acid). A much smaller hydrogen uptake was recorded in samples that contain large WO₃ crystallites (0.010 H/W, 15.6 W nm⁻²) and show the highest rate of formation of color centers. The formation of color centers in WO₃ crystallites is known to occur by both the accommodation of H atoms in the lattice and by the thermal desorption of oxygen which leaves behind a more closely packed structure (WO₃) that has a reduced charge and is therefore unable to accommodate the additional charge to make H⁺. As
a result, the sharp decrease in catalytic activity at high WO$_x$ surface densities may reflect the inability of large WO$_2$$_x$ domains to stabilize the additional electron required to accommodate H atoms as H$^{\circ}$, as well as a decrease in accessibility of the WO$_x$ species inside crystallites.

4. Conclusions

The domain size and structure of WO$_x$ species on ZrO$_2$ supports were determined for a wide range of WO$_x$ surface densities using UV−vis diffuse reflectance and Raman spectroscopies and CO$_2$ chemisorption. The WO$_x$ domain size is controlled only by WO$_x$ surface density and it is not influenced independently by WO$_x$ concentration, oxidation temperature, and ZrO$_2$ surface area. Three distinct regions of WO$_x$ coverage on ZrO$_2$ supports appear with increasing WO$_x$ surface density: a submonolayer region (0−4 W nm$^{-2}$), a polytungstate growth region (4−8 W nm$^{-2}$), and a polytungstate/crystalline WO$_x$ coexistence region (>8 W nm$^{-2}$). At low WO$_x$ surface densities, WO$_x$ species strongly interact with ZrO$_2$ and they remain isolated; as a result, they are difficult to reduce and contain few acid sites that can isomerize o-xylene at 523 K. At intermediate WO$_x$ surface densities, polytungstate domains grow with increasing WO$_x$ surface density, WO$_x$ species become easier to reduce, and o-xylene isomerization rates increase. At high WO$_x$ surface densities, o-xylene isomerization rates decrease because a significant fraction of the WO$_x$ species are found in the bulk of monoclinic WO$_3$ crystallites and are inaccessible to reactants.

The increase in o-xylene isomerization rates coincides with the growth of polytungstate species and a decrease in UV−vis absorption edge energy. This decrease in absorption edge energy reflects the condensation of WO$_x$ octahedra and the growth of WO$_x$ domains. Strong acid sites form on WO$_x$−ZrO$_2$ by the slight reduction of these polytungstate domains in the presence of H$_2$ at reaction temperatures (523 K). These H$^{\circ}$ sites (Brønsted acid) sites form on larger WO$_x$ domains because the electron from the H-atom may be delocalized throughout several neighboring octahedra.

WO$_x$−ZrO$_2$ samples containing crystalline WO$_3$ domains are less active per W atom because a fraction of the H atoms are accommodated inside the WO$_3$ crystals where they are inaccessible to hydrocarbon reactant molecules. In addition, crystalline WO$_3$ domains may reduce by loss of oxygen from the lattice, which would decrease the ability of these material to accept additional electrons from H atoms and form Brønsted acid sites.

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Nomenclature

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References and Notes

(1) Misono, M.; Okuhara, T. Chemtech 1993, 23 (11), 23.


