Catalysis science of the solid acidity of model supported tungsten oxide catalysts

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Abstract

A series of supported WO₃ catalysts were synthesized by incipient wetness impregnation of ammonium metatungstate aqueous solutions onto Al₂O₃, TiO₂, Nb₂O₅, and ZrO₂ supports as a function of tungsten oxide loading. The resulting solid acid catalysts were physically characterized with in situ Raman and UV–vis spectroscopy and chemically probed by methanol dehydration to dimethyl ether (CH₃OH-TPSR and steady-state CH₃OH dehydration). The molecular structures of the dehydrated supported tungsten oxide phase were determined to be monotungstate and polytungstate surface WOₓ species below monolayer surface coverage (<4.5 W/nm²), crystalline WO₃ nanoparticles (4.5–9 W/nm²) and large bulk-like WO₃ crystals (>9 W/nm²). The electronic structure for the different tungsten oxide species, Eₔ, was independent of the specific support and decreased monotonically with increasing tungsten oxide domain size (W/nm²). The solid acid catalytic activity, however, did not correlate with either the molecular or electronic structures because of the dominant contribution by the surface WOₓ species to the overall catalytic performance of the supported WO₃ catalysts and its reactivity dependence on the specific support. For supported WO₃/Al₂O₃, the surface WOₓ monolayer was more active than the crystalline WO₃ phases and, consequently, the TOF decreased with increasing surface W/nm² density. For tungsten oxide supported on Nb₂O₅, TiO₂ and ZrO₂, the surface WOₓ monolayer is less active than the crystalline WO₃ phases and, consequently, the TOF increases with surface W/nm² density. These reactivity trends reflect the influence of the specific support cation electronegativity on the acid character of the bridging W–O-Support bond.

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1. Introduction

Supported tungsten oxide catalysts consist of tungsten oxide overlayers on high surface area oxide supports (e.g., Al₂O₃, ZrO₂, TiO₂, etc.) [1–30]. The tungsten oxide overlay can be present as isolated surface monotonstages, polymeric surface polytungstates, crystalline WO₃ particles as well as form compounds with the oxide supports (e.g., Al₂(WO₄)₃, Zr(WO₄)₂, etc.). The supported tungsten oxide catalysts find numerous applications in the petroleum, chemical, and pollution control industries [31–33]: hydrodesulfurization (HDS) [34] and hydrocarbon cracking (WO₃/Al₂O₃) [35,36], selective catalytic reduction (SCR) of NOₓ with NH₃ to form N₂ (V₂O₅–WO₃/TiO₂) [37–39] alkenes isomerization (WO₃/TiO₂) [40,41] alkane isomerization (WO₃/ZrO₂) [15–17] and olefin metathesis (WO₃/SiO₂) [42]. For many of these catalytic applications, the solid acidity of the supported tungsten oxide phase plays a crucial role in their overall catalytic performance. For supported WO₃/Al₂O₃ catalysts, only surface Lewis acid sites are present at low surface coverage and surface Bronsted acid sites are also present at intermediate and high surface coverage [5,6,12]. Similar observations have been made for the surface acidity characteristics of supported WO₃/ZrO₂ [16,17,21], WO₃/TiO₂ [10,37,43] and WO₃/Nb₂O₅ [44]. At low surface tungsten oxide coverage (<2 W/nm²), surface polytungstate species predominate and only Lewis acid character is found to be present. At intermediate tungsten oxide surface coverage (3–4 W/nm²), surface polytungstate species become predominant and both Bronsted acid sites and Lewis acid sites are present. At higher tungsten oxide coverage (>4 W/nm²),...
crystalline WO₃ nanoparticles (NPs) are present on top of the surface tungsten oxide layer. The molecular level relationships of these different tungsten oxide structures and their surface acidic characteristics are not fully understood at present because of conflicting tungsten oxide structural assignments and the exact surface density where the close packed surface tungsten oxide monolayer forms [4–7,10–15,16–30].

Studies with well-defined model supported tungsten oxide catalysts were undertaken in the present study in order to investigate the (1) molecular and electronic structures of the surface monolayer tungstate species, surface polytungstate species and WO₃ NPs, (2) surface tungsten oxide density for close packed monolayer coverage, (3) surface acidity characteristics of the different tungsten oxide structures for methanol dehydration, and (4) the molecular/electronic structure–solid acidity relationship. The term ‘model’ in the present study refers to preformed supports that are already present in their stable oxide forms (e.g., Al₂O₃, ZrO₂, TiO₂ and Nb₂O₅) and are not present as metastable precursors (e.g., ZrO(OH)₂) that will undergo structural changes during the catalysis synthesis steps [8,9]. Comparison of such metastable ZrO(OH)₂ supports with preformed model ZrO₂ supports will be the subject of a future communication.

2. Experimental

2.1. Catalyst synthesis

The supported tungsten oxide catalysts were prepared by incipient wet impregnation of aqueous (NH₄)₁₀W₁₂O₄₁·5H₂O solutions on the different oxide supports: Al₂O₃ (Harshaw, 178 m²/g), TiO₂ (Degussa P-25, 51 m²/g), Nb₂O₅ (CBMM AD1927 HY-340, 66 m²/g), and ZrO₂ (Degussa, 60 m²/g). The impregnated samples were initially dried overnight at room temperature, dried at 110 °C for 2 h and then calcined in flowing air for 4 h at 450 °C. The surface tungsten oxide density, W/nm², was varied by both increasing the tungsten loading for the 450 °C calcined catalysts as well as sintering the oxide support by calcining at elevated temperatures (700, 800 and 900 °C) for an additional 2 h.

2.2. BET-specific surface area measurement

The BET surface areas of the samples were measured by physical adsorption of N₂ at 77 K (Quantachrome Corp., Model OS-9). The samples were outgassed at 250 °C prior to the N₂ adsorption (Quantachrome Corp., Model QT-3).

2.3. Raman spectroscopy

The molecular structure of the supported tungsten oxide phases was determined with Raman spectroscopy since this technique has the ability to discriminate between the different tungsten oxide molecular structures [2–5,7,11,13,14,19]. The Raman spectra were collected with a single monochromator Horiba-Jobin Yvon LabRam HR system employing 532 nm laser excitation (Spectra Physics Model 164, Yag doubled diode pumped laser, 20 mW) and possessing a LN CCD detector (JY-CCD3000V). The catalysts were dehydrated in an in situ cell (Linkam T1500) by flowing 10% O₂/He at 450 °C for 1 h, and cooled to room temperature before the spectra were collected.

2.4. UV–vis-NIR diffuse reflectance spectroscopy (DRS)

The electronic structure of the supported tungsten oxide phases was determined with UV–vis diffuse reflectance spectroscopy (Varian Cary 5E UV–vis-NIR spectrophotometer). An in situ cell (Harrick, HVC-DR2) was employed to dehydrate the supported tungsten oxide catalysts at 400 °C in flowing 10% O₂/He for 1 h, and the UV–vis spectra were collected after cooling the sample to room temperature. A magnesium oxide reference was used for the baseline standard. The Kubelka-Munk function F(R∞) was extracted from the UV–vis DRS absorbance and the edge energy (Eₐ) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of the plot of [F(R∞)] × hν in the low-energy rise of the plot of [F(R∞)] × hν [45]. In order to properly determine the Eₐ values of the WO₃ particles present above monolayer surface coverage, the spectrum for monolayer absorbance was background subtracted to ensure that only the electronic structure of the WO₃ particles was determined.

2.5. CH₃OH temperature-programmed surface reaction (TPSR) spectroscopy

The surface acidity properties of the supported tungsten oxide catalysts were chemically probed with CH₃OH-TPSR (Altamira AMI-200) equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). In the presence of surface acid sites, methanol dehydrates to yield CH₃OCH₃ (DME) [46]. The catalysts were pretreated at 400 °C in flowing 10% O₂/He for 40 min to dehydrate the samples and remove any possible oxidizable surface residues. The catalysts were subsequently cooled in the oxidizing environment to 110 °C, then switched to flowing He and further cooled to 100 °C. The methanol was chemisorbed at 100 °C by flowing a 2000 ppm CH₃OH/He mixture for 30 min. The catalyst was initially purged for 1 h in flowing He to remove any physically adsorbed CH₃OH and then the sample temperature was increased in flowing He at a heating rate of 10 °C/min. The resulting CH₃OCH₃ (mle = 45) TPSR spectra were analyzed to extract the surface kinetics of this first-order reaction that involves the rate-determining step of C–O scission of the surface methoxy intermediate [47]. The DME formation activation energy, Eₐ, was calculated with the first-order Redhead equation [48]:

\[
\frac{E_a}{RT_p^2} = \frac{v}{\beta^2} \exp \left( - \frac{E_a}{RT_p} \right)
\]

where \( T_p \) represents the TPSR peak temperature, \( v = 10^{13} \text{ s}^{-1} \) for first-order kinetics, \( \beta \) the heating rate (10 °C/min) and \( R \) is the gas constant. Determination of the \( E_a \) values allowed
3. Results and discussion

3.1. Molecular and electronic structures of model supported tungsten oxide catalysts

The Raman spectra of dehydrated supported WO₃/ZrO₂ catalysts are presented in Fig. 1 as a function of tungsten oxide loading (W/nm²). The Raman band appearing in the 990–1020 cm⁻¹ region is characteristic of the terminal W=O bond of the dehydrated surface WOₓ species and continuously shifts from 990 to 1020 cm⁻¹ with increasing tungsten oxide loading [13]. This shift of the Raman band parallels the continuous increase in the surface polytungstate/monotungstate ratio with increasing tungsten oxide loading (see UV–vis section below). This suggests that the surface monotungstate species exhibit a W=O vibration at ~990–1000 cm⁻¹ and the surface polytungstate species possess its W=O vibration at ~1020 cm⁻¹, and that the shift from ~990 to 1020 cm⁻¹ is related to the increasing surface polytungstate/monotungstate ratio with surface tungsten oxide coverage. The Raman bands of crystalline WO₃ NPs (805 and 715 cm⁻¹) begin to appear at ~4 W/nm², and continuously increase with increasing tungsten oxide loading. The appearance of crystalline WO₃ NPs generally signifies that a close packed monolayer of surface tungsten oxide has been achieved and that no additional exposed support sites remain for additional anchoring of surface WOₓ species to the support [4,14]. The absence of exposed support sites is further confirmed by CH₃OH chemisorption IR experiments that demonstrate that surface support-OCH₃ sites, as well as reactive support-OH sites, are not present at monolayer coverage and that only surface W–OCH₃ sites are present at monolayer and higher surface WOₓ coverage [47,49].

The surface tungsten oxide density for monolayer surface coverage can be quantified by plotting the intensity of the Raman band for the surface WOₓ species and normalizing it against the ZrO₂ support Raman band at ~480 cm⁻¹, an internal standard, as a function of W/nm². As can be seen in Fig. 2, the normalized intensity of the surface WOₓ species increases linearly with increasing tungsten oxide loading until ~4.5 W/nm² and remains constant at higher tungsten oxide loadings. Thus, monolayer surface coverage for surface WOₓ species on the model preformed ZrO₂ support is achieved at ~4.5 W/nm². Similar findings were also observed for the model supported WO₃/Al₂O₃, WO₃/TiO₂ and WO₃/Nb₂O₅ catalysts. This value of monolayer surface coverage for surface WOₓ species has always been reported in the catalysis literature for such model supported tungsten oxide catalysts [2,4,5,7,10,11,13,18,20,25–28,43,44].

The UV–vis E₉ values for the dehydrated supported WO₃/ZrO₂ catalysts are presented in Fig. 3 as a function of tungsten oxide loading. The E₉ values continuously decreases with increasing surface WOₓ coverage. At the lowest W/nm² surface density, the E₉ value is ~4.5 eV and is similar to the value for
reference compounds possessing isolated WO$_4$ or WO$_6$ structures (e.g., Na$_2$WO$_4$, NiWO$_4$, respectively) [47]. At a surface density of 4.5 W/nm$^2$, monolayer surface coverage, an $E_g$ value of $\sim$4.2 eV is obtained and corresponds to the value found for reference compounds consisting of polymeric WO$_3$ chains (e.g., Na$_2$W$_2$O$_7$, which consists of alternating WO$_4$ and WO$_6$ units) [47]. Above 4.5 W/nm$^2$, the $E_g$ values continue to decrease with increasing tungsten oxide loading until about 9 W/nm$^2$. This continuous decrease from 4.5 to 9 W/nm$^2$ is related to the presence of the crystalline WO$_3$ NPs present above monolayer surface coverage, which is consistent with the Raman results presented above. The $E_g$ values for the WO$_3$ NPs, however, are higher than that for bulk WO$_3$ ($E_g = 2.8$ eV) because of the quantum confinement effect of these small nanoparticles. Above 9 W/nm$^2$, the $E_g$ value is relatively constant and close to the value for large bulk WO$_3$ particles that are present at such high surface WO$_3$ density. The surface WO$_3$ density on ZrO$_2$ could also be varied by raising the calcination temperature, which resulted in sintering the ZrO$_2$ support and, consequently, increasing the surface W density. The $E_g$ values for such a series of supported WO$_3$/ZrO$_2$ catalysts calcined at elevated temperatures are also plotted in Fig. 3 and also fall on the same curve as a function of surface W density. Furthermore, the $E_g$ values for supported WO$_3$/Al$_2$O$_3$ catalysts as a function of tungsten oxide loading are also shown in Fig. 3 and their values exactly overlay those of the supported WO$_3$/ZrO$_2$ catalyst system as a function of W/nm$^2$. The strong UV–vis absorption by the TiO$_2$ and Nb$_2$O$_5$ supports prevents the accurate determination of the $E_g$ values for the supported tungsten oxide phases on these supports. Thus, the $E_g$ value only depends on the surface W density and is related to the molecular structure of the supported tungsten oxide phase.

In summary, the surface tungsten oxide phases on the examined supports consist of (i) isolated surface monotungstate and polytungstate species below monolayer surface coverage (<4.5 W/nm$^2$) with increasing poly/mono ratio with loading in this region, (ii) crystalline WO$_3$ NPs (4.5 $< W < 9$ W/nm$^2$), and large, bulk-like WO$_3$ particles (>9 W/nm$^2$). Previous XANES structural studies revealed that the dehydrated surface WO$_3$ species on model supports at low surface coverage tend to be present in WO$_4$ coordination at low surface coverage and WO$_5$/WO$_6$ coordination at high surface coverage [7,10]. Comparison with the current UV–vis and Raman data reveals that the isolated surface mononitrogstate species possess WO$_4$ coordination and the surface polytungstate species possess WO$_5$/WO$_6$ coordination. Furthermore, the Raman shift from $\sim$990 to 1020 cm$^{-1}$ with surface WO$_3$ coverage suggests that the surface mononitrogstate WO$_4$ species are probably dioxo (O=W=O) structures and that the surface polytungstate WO$_5$/WO$_6$ species are probably monooxo (W=O) structures because dioxo functionalities generally vibrate $\sim$20–30 cm$^{-1}$ lower than monooxo functionalities [50].

3.2. Surface reactivity of model supported tungsten oxide catalysts

The surface acidic properties of the supported tungsten oxide phase were chemically probed with CH$_3$OH dehydration to CH$_3$OCH$_3$ (DME) since this reaction is known to readily proceed over surface acidic sites [46]. The methanol dehydration reaction, unfortunately, does not discriminate between surface Lewis and Bronsted acid sites, which require the use of basic chemical probe molecules. Nevertheless, the methanol dehydration reaction provides fundamental information about the number of catalytic active sites and their relative acidic activity. Recent studies have revealed that this catalytic reaction proceeds via first-order kinetics where the rate-determining step is breaking of the C–O bond of the surface CH$_3$O* intermediate [47]. All the supported tungsten oxide catalysts were found to almost exclusively yield DME as the reaction product, which reflects the acidic nature of the supported tungsten oxide phase.

The CH$_3$OH-TPSR experiments demonstrated that bulk WO$_3$ ($T_p$,W = 254 °C) has significantly more catalytic active surface acid sites than found on the pure oxide supports ($T_p$, Zr = 374 °C, $T_p$, Ti = 325 °C, $T_p$, Nb = 300 °C) with the exception of Al$_2$O$_3$ ($T_p$, Al = 196 °C). The surface tungsten oxide phase on all the supports, with the exception of Al$_2$O$_3$, introduced much more active surface acid sites to the catalysts with resulting significantly lower $T_p$ values. In the case of surface WO$_3$ on Al$_2$O$_3$, monolayer surface WO$_3$ coverage resulted in the complete suppression of the very active DME $T_p$ peak at 196 °C from the alumina support sites and the appearance of a less active DME $T_p$ peak at $\sim$219–226 °C from the surface WO$_3$ species. The CH$_3$OH-TPSR chemical probe findings are in agreement with the CH$_3$OH-IR findings that no exposed surface Al$_2$O$_3$ sites are present above monolayer surface coverage for the supported WO$_3$/Al$_2$O$_3$ catalyst system. This is consistent with the concept of a closed packed monolayer of surface WO$_3$ species that do not expose any support cations [51,52]. Consequently, the catalytic acid sites being probed by CH$_3$OH-TPSR above monolayer surface coverage are exclusively associated with the supported tungsten oxide phase and not with exposed support surface sites.

The CH$_3$OH-TPSR chemical reactivity results for the supported WO$_3$/ZrO$_2$ catalysts are presented in Fig. 4 as a
function of tungsten oxide loading where the $T_p$ values have been converted to first-order $k_{ads}$ values employing the Redhead equation. Although exposed surface Zr sites are present below monolayer surface coverage, they do not contribute to the kinetic results because the surface WO$_x$ species are significantly more active than the exposed ZrO$_2$ sites for DME production ($T_p$, Zr = 374 °C and $T_p$, W = 254 °C). The CH$_3$OH-TPSR chemical probe experiments reveal that the acidic catalytic activity of the supported WO$_3$ catalysts increases with increasing surface tungsten oxide density, and asymptotically approaches that of bulk WO$_3$ above 9 W/nm$^2$. The same exact trends and asymptotic values were also obtained for the supported WO$_3$/TiO$_2$ and WO$_3$/Nb$_2$O$_5$ catalysts. An inverse trend, however, was found for the supported WO$_3$/Al$_2$O$_3$ catalysts with the $k_{ads}$ monotonically decreasing with increasing surface coverage above monolayer (>4.5 W/nm$^2$) and asymptotically approaching that of bulk WO$_3$ above 9 W/nm$^2$ (see Fig. 4). The supported WO$_3$/Al$_2$O$_3$ catalyst system was not investigated below monolayer coverage because active exposed Al$_2$O$_3$ surface sites would overshadow the catalytic activity of the supported WO$_3$ catalysts.

The CH$_3$OH-TPSR spectra also allowed for determination of the number of exposed surface WO$_x$ sites, $N_s$, in the catalysts since the areas under their curves directly reflected this value. The supported WO$_3$ catalysts’ $N_s$ values were normalized to those obtained for ~4.5 W/nm$^2$ for each support since these catalysts possessed 100% dispersed surface tungsten oxide and their $N_s$ values are quantitatively known. The $N_s$ values are shown in Fig. 5 for supported WO$_3$/ZrO$_2$ and linearly increase from 0 to 4.5 W/nm$^2$ (by definition since the WO$_3$ is 100% dispersed until monolayer), gently decrease in the 4.5–9 W/nm$^2$ range, and rapidly decrease above 9 W/nm$^2$. Similar $N_s$ trends with W/nm$^2$ surface density were also observed with the other supported WO$_3$ catalysts above monolayer surface coverage.

Steady-state methanol dehydration catalytic studies to DME were also undertaken and the TOF values for the different catalysts are presented in Fig. 6 as a function of tungsten oxide loading and specific oxide support. The reaction rates were converted to TOF values by employing the $N_s$ values determined from the CH$_3$OH-TPSR investigation. The TOF values for the supported WO$_3$/ZrO$_2$, WO$_3$/TiO$_2$ and WO$_3$/Nb$_2$O$_5$ catalysts increase with increasing surface tungsten oxide density up to ~9 W/nm$^2$ and then leveled off. For the supported WO$_3$/Al$_2$O$_3$ catalyst system, an inverse trend was found where the TOF value slightly decreases with increasing surface tungsten oxide density up to ~9 W/nm$^2$ and then levels off with increasing surface W density.

### 3.3. Molecular/electronic structure–acidity relationships

The molecular structures of the supported tungsten oxide phases were shown to be identical for the catalyst systems investigated: isolated surface monotungstate dioxo WO$_4$ species at low surface coverage (<4.5 W/nm$^2$), polymeric surface polytungstate monoxo WO$_5$/WO$_6$ species also present at higher surface coverage (<4.5 W/nm$^2$), with the polytungstate being the dominant surface WO$_x$ species at monolayer and higher surface coverage, WO$_3$ NPs between 4.5 and 9 W/nm$^2$, and large bulk-like WO$_3$ particles above 9 W/nm$^2$. It should be noted that the WO$_3$ crystallites were usually present above monolayer surface coverage and were formed on top of the surface WO$_x$ monolayer. Furthermore, exposed support surface sites are not present for monolayer and higher surface WO$_x$ coverage because the reactive support-OH sites are consumed by the surface WO$_x$ species and support-OCH$_3$ species are not detected at monolayer surface WO$_x$ coverage (~4.5 W/nm$^2$).

![Fig. 5. Number of exposed W sites/nm$^2$ for supported WO$_3$/ZrO$_2$ catalysts as a function of surface W density (W/nm$^2$). Monolayer surface coverage, 4.5 W/nm$^2$, is represented by the vertical dashed line.](image)

![Fig. 6. CH$_3$OH dehydration TOF values for different supported WO$_3$ catalyst systems as well as the TOF for bulk WO$_3$ as a function of surface W density (W/nm$^2$). Monolayer surface coverage, 4.5 W/nm$^2$, is represented by a vertical dashed line.](image)
The corresponding electronic structures of the different tungsten oxide structures reflect their domain size: monotungstate $<$ polytungstate $<$ WO$_3$ NP $<$ bulk-like WO$_3$ particle. The $E_g$ value reflects the degree of electron delocalization in the tungsten oxide phase and decreases with increasing tungsten oxide domain size. Consequently, larger tungsten oxide domains allows for greater electron delocalization. The methanol dehydration first-order $k_{\text{rdns}}$ reaction rate constant is plotted versus $E_g$ for the supported WO$_3$/ZrO$_2$ and WO$_3$/Al$_2$O$_3$ catalysts in Fig. 7. As mentioned earlier, the $E_g$ values for the supported WO$_3$/TiO$_2$ and WO$_3$/Nb$_2$O$_5$ catalyst systems could not be determined because of the strong UV–vis absorption by these oxide supports. For the supported WO$_3$/ZrO$_2$ catalyst system, the $k_{\text{rdns}}$ reaction rate constant increases with surface tungsten oxide density while the electronic $E_g$ values decrease. The opposite is trend is observed for the $k_{\text{rdns}}$ reaction rate for supported WO$_3$/Al$_2$O$_3$. The curves in Fig. 7 demonstrate that no unique relationship can be established between the methanol dehydration $k_{\text{rdns}}$ and the electronic structure of the different tungsten oxide domains because of the complete opposite variations of the two curves. Similar trends are also obtained when TOF is plotted versus $E_g$. Thus, another explanation must be responsible for these trends.

The one structural parameter that is uniquely different for all the investigated supported WO$_3$ catalysts is the different oxide supports. The surface WO$_3$ species on Al$_2$O$_3$ are significantly more active than the surface WO$_3$ species on the oxide supports. The high electronegativity of the Al ligand results in a less basic or more acidic bridging W–O–Al bond [53]. The lower electronegativity of the other support cations, makes the bridging W–O–M bonds more basic or less acidic. The enhanced catalytic acidity of the surface WO$_3$ species on Al$_2$O$_3$ results in this tungsten oxide structure being more active than the WO$_3$ NPs and bulk-like WO$_3$ particles. The relatively low catalytic acidity of the surface WO$_3$ species on ZrO$_2$, TiO$_2$ and Nb$_2$O$_5$ makes this tungsten oxide structure somewhat less active than the WO$_3$ NPs and bulk-like WO$_3$ particles. Thus, it is the relative catalytic acidity of the surface WO$_3$ species, which is controlled by the specific support, that determines the activity trend as a function of surface W density in going from surface WO$_3$ to WO$_3$ NPs to bulk-like WO$_3$ particles.

4. Conclusion

A series of supported WO$_3$ catalysts were synthesized on Al$_2$O$_3$, Nb$_2$O$_5$, TiO$_2$ and ZrO$_2$ supports as a function of tungsten oxide loading. The molecular structure and monolayer surface coverage of the supported tungsten oxide phase was determined with UV–vis and Raman spectroscopy, respectively. The same tungsten oxide species were found to be present on all the supports as a function of surface tungsten oxide density (W/nm$^2$) with monolayer surface coverage corresponding to 4.5 W/nm$^2$: surface monometal tungstate WO$_4$ species ($<$ 4.5 W/nm$^2$), surface polytungstate WO$_5$/WO$_6$ species ($<$ 4.5 W/nm$^2$), WO$_3$ NPs (4.5–9 W/nm$^2$), and large bulk-like WO$_3$ particles ($>$ 9 W/nm$^2$). The edge energy ($E_g$) of all the supported tungsten oxide catalysts monotonically decreased with increasing tungsten oxide domain size (W/nm$^2$) indicating greater electron delocalization. The specific solid acidity of the supported tungsten oxide catalysts, however, was not found to correlate with either the tungsten oxide molecular structures or electronic structures. This was a consequence of the acidic catalytic activity of the surface monometal tungstate and polytungstate species relative to the WO$_3$ NPs and the bulk-like WO$_3$ particles. For the supported WO$_3$/Al$_2$O$_3$ catalyst system, the surface WO$_3$ species are more active than the crystalline WO$_3$ particles and, consequently, the overall specific acidic catalytic activity (TOF) decreases with increasing surface W/nm$^2$ density as WO$_3$ NPs are introduced. For the other supported WO$_3$ catalyst systems (WO$_3$/Nb$_2$O$_5$, WO$_3$/TiO$_2$ and WO$_3$/ZrO$_2$), the surface WO$_3$ species are less active than the crystalline WO$_3$ particles and, consequently, the overall specific acidic catalytic activity (TOF) increases with increasing surface W/nm$^2$ density as WO$_3$ NPs are introduced. Consequently, no universal molecular/electronic structure–solid acidity relationships exist for supported WO$_3$ catalysts.

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