New insights into the nature of the acidic catalytic active sites present in ZrO2-supported tungsten oxide catalysts

Elizabeth I. Ross-Medgaarden a, William V. Knowles b, Taejin Kim a, Michael S. Wong b,c, Wu Zhou d, Christopher J. Kiely d, Israel E. Wachs a,*

a Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA
b Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, USA
c Department of Chemistry, Rice University, Houston, TX 77005, USA
d Center for Advanced Materials and Nanotechnology, Department of Materials Science & Engineering, Lehigh University, Bethlehem, PA 18015, USA

Received 10 January 2008; revised 4 March 2008; accepted 5 March 2008

Available online 10 April 2008

Abstract

An extensive series of supported WO3/ZrO2(OH)x−2x catalysts (WZrOH) were synthesized by standard aqueous impregnation of ammonium metatungstate into an amorphous ZrO2(OH)x−2x metastable support, followed by high-temperature calcination (at 773–1173 K). The supported WZrOH catalysts were also compared with well-defined model supported WO3/ZrO2 catalysts (WZrO2) consisting of a thermally stable crystalline m-ZrO2 support. Both series of supported tungsten oxide catalysts were physically characterized (by XRD, XPS, TEM, in situ Raman, and in situ UV–vis spectroscopy) and chemically probed by methanol dehydration (i.e., TPSR spectroscopy and steady-state catalytic studies). Monolayer surface WO x coverage was found to occur at ~4.5–5 W-atoms/nm2 for both catalytic systems. Whereas the dehydrated model supported WZrO2 series contained only surface WO x species below monolayer coverage, the dehydrated supported WZrOH series had the same surface WO x species, as well as some Zr-stabilized distorted WO3 nanoparticles (NPs). Above monolayer coverage, the model supported WZrO2 catalysts contained only ordered crystalline WO3 NPs, but the supported WZrOH catalysts had both ordered WO3 NPs and Zr-stabilized distorted WO3 NPs. The comparative methanol dehydration to dimethyl ether acidity study revealed that the Zr-stabilized distorted WO3 NPs were the catalytic active sites in supported WZrOH catalysts. These findings represent a new model for the origin of the enhanced solid acidity of supported WZrOH catalysts.

© 2008 Elsevier Inc. All rights reserved.

Keywords: Catalysts, supported, oxides, WO3, ZrO2; Reaction, CH3OH, dehydration, CH3OCH3, DME; Spectroscopy, in situ, Raman, UV–vis, XPS; Electron microscopy, TEM, HREM imaging

1. Introduction

Zirconia-supported tungsten oxide catalysts have received much attention in the recent catalysis literature due to their industrial application for converting C4–C8 paraffins to highly branched species that upgrade the gasoline octane number [1–11]. Supported WOx/ZrO2 catalysts also show commercial promise for such major industrial applications as selective catalytic reduction of NOx to N2 [12,13], xylene formation from toluene and methanol [14], oligomerization of <C20 alkanes to gasoline, diesel and lubricants (C30+) [15], and the removal of sulfur- and nitrogen-containing impurities (“hydrotreating”) from hydrocarbon streams when combined with a hydrogenation/dehydrogenation component, such as Pt [16]. For many of these catalytic applications, the solid acidity of the supported tungsten oxide phase plays a crucial role in the overall catalytic performance.

There seems to be a general agreement in the literature that the maximum reactant turnover rates occur at “intermediate” surface tungsten densities (W-atoms/nm2): ~6–8 W/nm2 for n-pentane isomerization [2,17], and ~7–8 W/nm2 for o-xylene isomerization [18–20], as well as 2-butanol dehydration [21]. “Intermediate” is loosely defined as the W/nm2 range that
maximizes the population of amorphous surface polytungstate species relative to isolated surface WO$_3$ and WO$_3$ nanocrystalline domains. Absolute values for the minimum and maximum surface densities that bracket this range differ between reactions and even differ within a given reaction, depending on operating conditions and the basis of measurement. Most researchers agree that regardless of the exact numerical W/\(\text{nm}^2\) value, the effective upper end of the “intermediate” range corresponds to the formation of WO$_3$ nanocrystallites.

Multiple catalytic active sites have been proposed for supported WO$_3$/ZrO$_2$ catalysts [2,17–19,22,23], but supporting information for the nature of the true catalytic active phase is lacking. Most previous studies used a wide variety of characterization techniques and catalytic testing to describe the composition, oxidation state, coordination and nature of acidity (Brunsted vs Lewis) of the tungsten oxide species participating as the catalytic active sites. The following catalytic active site models have been proposed: (i) fully oxidized, noncrystalline surface polytungstate networks incorporating trace levels of surface-exposed Zr capable of stabilizing delocalized protons (Brunsted acidity) similar to that of heteropolyacids [17,25]; (ii) highly polymerized oxyanions of slightly reduced tungsten oxide formed in situ to stabilize delocalized protons (Brunsted acidity) on \(\text{H}^{4+}(\text{O}_3)^{6-}\) domains [18–21,23,24,26,27]; and (iii) catalysts with intermediate tungsten oxide loadings that generate nearly a 1:1 ratio of strong Brunsted acid sites to Lewis acid sites, although the origin of the surface acid sites (W or Zr cations) is not known [2,28,29].

Based on the trend of reactivity versus tungsten oxide structure, the growing literature consensus is that the catalytic active site(s) responsible for high surface acidic activity form with a maximum in surface polytungstate (WO$_3$) concentration. The maximum amount of surface polytungstate species should occur at monolayer surface tungsten oxide coverage, but very different models for surface polytungstate monolayer coverage have been proposed. The support layer geometry monolayer (ML) models assume epitaxial-like growth of the surface tungsten oxide overlayer without considering possible chemical interactions (e.g., coordination, steric hindrance, repulsion) at the surface layer. Based on the (001) projection of ZrO$_2$ [30], a tungstate ML was calculated as \(\sim 7.3\) W-atoms/\(\text{nm}^2\) [2,31], in which the WO$_6$ octahedra are presumably anchored to exposed Zr–OH sites [32]. Other models concentrate on the surface layer geometry and are support-independent, disregarding how the surface tungsten oxide species and the underlying support oxide are bound together [22,33–35]. One such model envisions surface saturation of the supported metal oxide layer as a two-dimensional close packing of monomeric sites [22,33–35]. For bulk WO$_3$, a close packing was calculated as \(0.21\) g WO$_3$/\(100\) m$^2$, which is equivalent to \(\sim 5.5\) W-atoms/\(\text{nm}^2\) [33–36]. Another model estimates surface saturation of the WO$_3$ at \(\sim 6.4\) W-atoms/\(\text{nm}^2\) based on the bulk density of WO$_3$ [25], and yet another model estimates the ML at \(\sim 7.8\) W-atoms/\(\text{nm}^2\) by estimating the density of WO$_3$ species in a two-dimensional plane of corner-shared WO$_6$ octahedra [2].

In contrast to the foregoing “theoretical” ML models that assume a specific structure for a surface tungsten oxide species, experimental XPS, ISS, and Raman spectroscopic measurements have demonstrated that ML coverage actually corresponds to 4–5 W-atoms/\(\text{nm}^2\) [36–38] for surface WO$_3$ on all oxide supports, with the exception of the weakly interacting supported WO$_3$/SiO$_2$ catalyst system, where tungsten oxide dispersion is very poor. The foregoing literature review of supported WO$_3$/ZrO$_2$ catalysts reveals a lack of agreement concerning several critical issues regarding the tungstated zirconia system. Despite several papers devoted to the physical and chemical characterization of supported WO$_3$/ZrO$_2$ catalysts, the issues of surface tungsten oxide ML coverage and the nature of the catalytic active acidic sites remain unresolved.

The present investigation was undertaken to investigate the structure–property relationship of supported WO$_3$/ZrO$_2$ catalytic materials and their acidic characteristics for methanol dehydrogenation. The study used zirconium oxyhydroxide supported tungsten oxide to (i) identify the surface WO$_3$ molecular structures present on ZrO$_2$ as a function of surface W/\(\text{nm}^2\) density, (ii) determine the surface W/\(\text{nm}^2\) density corresponding to surface WO$_3$ monolayer coverage on ZrO$_2$, (iii) investigate the surface acid catalysis of supported WO$_3$/ZrO$_2$ with the methanol chemical probe molecule, and (iv) identify the nature of the catalytic active site(s) present for supported WO$_3$/ZrO$_2$ catalysts. The findings with zirconium oxyhydroxide-supported tungsten oxides (WZrOH) are also critically compared with the previously published findings for the model supported WO$_3$/ZrO$_2$ system (WZrO$_2$), in which the starting ZrO$_2$ support is already present as a crystalline material [37,38].

2. Experimental

2.1. Catalyst synthesis

2.1.1. Preparation of the ZrO$_4$(OH)$_{4−2x}$ support

Zirconium oxyhydroxide was prepared by a method similar to that described by Hino and Arata [1]. A completely dissolved solution of 313.3 g ZrOCl$_2$·8H$_2$O (Aldrich, 98%) in 0.7 L of deionized water (room temperature, final solution pH \(11\)) was added dropwise over \(\sim 1\) h into 600 mL of deionized water, with 15.8 M of NH$_3$H$_2$O added as necessary to maintain batch pH 10 for 30 min before separation. Multiple redispersions and filtrations were performed until the supernatant chloride ion concentration reached that of the water background, as verified by AgNO$_3$ titration with K$_2$Cr$_2$O$_7$ indicator. Finally, the powder was dried overnight in static air at 343 K before being crushed and sieved (to \(< 170\) mesh).

2.1.2. Preparation of supported WO$_3$/ZrO$_4$(OH)$_{4−2x}$

The ZrO$_4$(OH)$_{4−2x}$ support was hand-mixed for \(\sim 1\) h after sieving to \(< 170\) mesh to homogenize the master batch. Before incipient wetness impregnation, the support was dried
overnight in static air at 343 K to remove adventitious moisture. Tungstated-zirconia catalysts with various weight percentages (5.1, 10.1, 15, 19.5, 23.3, and 26.6%) were prepared by incipient-wetness impregnation of aqueous solutions of ammonium metatungstate (NH₄)₁₀W₁₂O₄₁·5H₂O (Osrarn Sylvania, 98% purity). The zirconia hydroxide support sample was impregnated to 95% pore volume (Vₚ) as determined by triple nitrogen physisorption analyses at 77 K (Vₚ at P/P₀ = 0.984, Micromeritics ASAP2010) and mixed for ~30 min by hand to ensure uniform solution dispersion, with an average of Vₚ = 0.17 cm³/g. The tungstated zirconia samples were dried overnight at 343 K in static air, crushed, and sieved (to <170 mesh), then calcined at the desired temperature (773, 873, 973, 1073, and 1173 K) in static air for 3 h. The following notation is used to express the tungsten oxide samples: yWZrOH-T(ρₖ,surf), where y is the loading of W as WO₃ (wt%), T is the calcination temperature (K), ρₖ,surf is the tungsten surface density (W-atoms/nm²), and ZrOH represents the amorphous zirconium oxyhydroxide (ZrO₂(OH)₄–2x) support precursor used. For example, 10.1WZrOH-1073(6.2) designates a WO₃/ZrO₂(OH)₄–2x sample with 10.1% W that was calcined to 1073 K with a resulting ρₖ,surf of 6.2 W-atoms/nm². Surface tungsten oxide coverage and loading for the supported WO₃ catalysts are specified in Table 1. The ρₖ,surf for the WZrOH catalysts is based on a more general definition of surface density that uses the combined material surface area (i.e., the surface area of the calcined sample), because the amorphous ZrO₂(OH)₄–2x support is sensitive to calcination temperatures. Because significant structural rearrangement and consequent loss of surface area occurred for WO₃/ZrO₂(OH)₄–2x materials, the resulting ρₖ,surf of WZrOH and WZrO₂ catalysts discussed, are determined by the following equation:

\[
\rho_{\text{k,surf}} \left[ \frac{\text{M atoms}}{\text{nm}^2 \text{ support}} \right] = \left\{ \frac{1 \text{ [g catalyst]}}{\text{S.A. catalyst sample after calcination}} \right\} \times \left\{ \frac{1 \text{ [g catalyst]}}{\text{g support}} \right\} \times \left( 6.022 \times 10^{23} \frac{\text{mol M}}{\text{g MO}_x} \right) \left( \frac{v_{\text{stoich}}}{1} \frac{\text{mol M}}{\text{mol MO}_x} \right) \left( \frac{1 \text{ [M atoms]}}{\text{mol M}} \right) \left( \frac{10^9 \left[ \frac{\text{nm}^2}{\text{m}^2} \right]}{1} \right)^2.
\]

2.1.3. Preparation of model supported WO₃/ZrO₂ catalysts

The support used for the model supported WO₃/ZrO₂ catalysts was ZrO₂ (Degussa, BET = 60 m²/g), which is known to have a well-crystallized monoclinic structure. Tungsten oxide-supported zirconia catalysts with varying surface densities were prepared by incipient-wetness impregnation of aqueous solutions of ammonium metatungstate, (NH₄)₁₀W₁₂O₄₁·5H₂O (Pfaltz & Bauer, 99.5% purity) on the ZrO₂ support. The samples were first dried overnight under ambient conditions and then calcined in flowing air (Airgas, Zero Grade) at 723 K for 4 h. The following notation is used to express the supported tungsten oxide samples: xWZrO₂-T(ρₖ,surf), where x is the loading of W as WO₃ (wt%), T is the calcination temperature (K), ρₖ,surf is the tungsten surface density (W-atoms/nm²), and ZrO₂ represents the crystalline ZrO₂ support. For example, 9.4WZrO₂-723(4.5) designates a model WO₃/ZrO₂ sample with 9.4% W that was calcined to 723 K with a resulting ρₖ,surf of 4.5 W-atoms/nm². Surface tungsten oxide coverage and loading for the model supported WO₃ catalysts have been published previously [37,38]. Although it was previously shown [37,38] that the crystalline ZrO₂ support exhibits negligible surface area loss with the impregnation of surface WO₃, the surface densities for the model supported WZrO₂ catalysts in this work are based on the calcined sample’s final surface area, to be consistent with the surface density values reported for the supported WZrOH catalytic system.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>WO₃ (wt%)</th>
<th>T calcination (K)</th>
<th>BET S.A. (m²/g)</th>
<th>ρₖ,surf (W-atoms/nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1WZrOH-773(1.7)</td>
<td>5.1</td>
<td>773</td>
<td>75.8</td>
<td>1.7</td>
</tr>
<tr>
<td>5.1WZrOH-873(2.6)</td>
<td>5.1</td>
<td>873</td>
<td>51.6</td>
<td>2.6</td>
</tr>
<tr>
<td>5.1WZrOH-973(3.5)</td>
<td>5.1</td>
<td>973</td>
<td>37.5</td>
<td>3.5</td>
</tr>
<tr>
<td>5.1WZrOH-1073(4.3)</td>
<td>5.1</td>
<td>1073</td>
<td>30.7</td>
<td>4.3</td>
</tr>
<tr>
<td>5.1WZrOH-1173(5.9)</td>
<td>5.1</td>
<td>1173</td>
<td>22.6</td>
<td>5.9</td>
</tr>
<tr>
<td>10.1WZrOH-773(2.9)</td>
<td>10.1</td>
<td>773</td>
<td>89.1</td>
<td>2.9</td>
</tr>
<tr>
<td>10.1WZrOH-873(3.9)</td>
<td>10.1</td>
<td>873</td>
<td>66.5</td>
<td>3.9</td>
</tr>
<tr>
<td>10.1WZrOH-973(5.2)</td>
<td>10.1</td>
<td>973</td>
<td>50.3</td>
<td>5.2</td>
</tr>
<tr>
<td>10.1WZrOH-1073(6.2)</td>
<td>10.1</td>
<td>1073</td>
<td>42.1</td>
<td>6.2</td>
</tr>
<tr>
<td>10.1WZrOH-1173(9.8)</td>
<td>10.1</td>
<td>1173</td>
<td>26.9</td>
<td>9.8</td>
</tr>
<tr>
<td>15WZrOH-773(4.1)</td>
<td>15.0</td>
<td>773</td>
<td>96.0</td>
<td>4.1</td>
</tr>
<tr>
<td>15WZrOH-873(4.9)</td>
<td>15.0</td>
<td>873</td>
<td>80.0</td>
<td>4.9</td>
</tr>
<tr>
<td>15WZrOH-973(6.2)</td>
<td>15.0</td>
<td>973</td>
<td>62.8</td>
<td>6.2</td>
</tr>
<tr>
<td>15WZrOH-1073(8.4)</td>
<td>15.0</td>
<td>1073</td>
<td>46.2</td>
<td>8.4</td>
</tr>
<tr>
<td>15WZrOH-1173(15.8)</td>
<td>15.0</td>
<td>1173</td>
<td>24.7</td>
<td>15.8</td>
</tr>
<tr>
<td>19.5WZrOH-773(4.1)</td>
<td>19.5</td>
<td>773</td>
<td>123</td>
<td>4.1</td>
</tr>
<tr>
<td>19.5WZrOH-873(5.5)</td>
<td>19.5</td>
<td>873</td>
<td>91.4</td>
<td>5.5</td>
</tr>
<tr>
<td>19.5WZrOH-973(6.7)</td>
<td>19.5</td>
<td>973</td>
<td>75.2</td>
<td>6.7</td>
</tr>
<tr>
<td>19.5WZrOH-1073(10.6)</td>
<td>19.5</td>
<td>1073</td>
<td>47.9</td>
<td>10.6</td>
</tr>
<tr>
<td>19.5WZrOH-1173(20.2)</td>
<td>19.5</td>
<td>1173</td>
<td>25.1</td>
<td>20.2</td>
</tr>
<tr>
<td>23WZrOH-773(5.4)</td>
<td>23.0</td>
<td>773</td>
<td>113</td>
<td>5.4</td>
</tr>
<tr>
<td>23WZrOH-873(7.1)</td>
<td>23.0</td>
<td>873</td>
<td>85.7</td>
<td>7.1</td>
</tr>
<tr>
<td>23WZrOH-973(9.5)</td>
<td>23.0</td>
<td>973</td>
<td>63.6</td>
<td>9.5</td>
</tr>
<tr>
<td>23WZrOH-1073(14.0)</td>
<td>23.0</td>
<td>1073</td>
<td>43.1</td>
<td>14.0</td>
</tr>
<tr>
<td>23WZrOH-1173(24.1)</td>
<td>23.0</td>
<td>1173</td>
<td>25.1</td>
<td>24.1</td>
</tr>
<tr>
<td>26.6WZrOH-773(7.1)</td>
<td>26.6</td>
<td>773</td>
<td>97.8</td>
<td>7.1</td>
</tr>
<tr>
<td>26.6WZrOH-873(9.0)</td>
<td>26.6</td>
<td>873</td>
<td>76.8</td>
<td>9.0</td>
</tr>
<tr>
<td>26.6WZrOH-973(12.0)</td>
<td>26.6</td>
<td>973</td>
<td>57.4</td>
<td>12.0</td>
</tr>
<tr>
<td>26.6WZrOH-1073(17.1)</td>
<td>26.6</td>
<td>1073</td>
<td>40.5</td>
<td>17.1</td>
</tr>
<tr>
<td>26.6WZrOH-1173(29.4)</td>
<td>26.6</td>
<td>1173</td>
<td>23.5</td>
<td>29.4</td>
</tr>
</tbody>
</table>
2.2. Catalyst characterization

2.2.1. Elemental analysis

The elemental composition of select representative samples was measured via inductively coupled plasma–mass spectrometry (ICP-MS) at Lehigh Testing Laboratories, Inc. (New Castle, DE) for calculation of the final wt% WO₃ loading. Excellent agreement was found between nominal and actual wt% WO₃ loadings.

2.2.2. BET specific surface area

The BET surface areas of the samples were determined by a 5-point BET correlation (P/P₀ = 0.06, 0.08, 0.12, 0.16, and 0.20) [41] for N₂ adsorption isotherms (77 K) collected on a Micromeritics ASAP 2010 using Matheson ultra-high-purity (UHP) N₂. Sample pretreatment involved evacuation at 523 K until the degas rate was <3 × 10⁻³ mm Hg/min. The instrument accuracy is approximately ±1.3% (relative standard deviation, n = 44) of measured value, with the instrument calibration verified by a SiO₂/Al₂O₃ reference standard.

2.2.3. X-ray diffraction

Powder X-ray diffraction (XRD) patterns were obtained with a powder diffractometer (Rigaku D/Max-2100 PC) using unfiltered CuKα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. Diffraction patterns were collected in continuous scan mode using a 0.02° step size and a ~2.5 s/step scan rate. Goniometer alignment was verified by daily analysis of a Rigaku-supplied polycrystalline silicon reference standard.

For the pseudobinary combination of t-ZrO₂ and m-ZrO₂, an empirical relationship was used to estimate the relative volume fractions (Vᵢ) of the two crystalline species (Vₘ + Vₜ = 1) using the integrated areas (I) of the (111) and (111) reflections for m-ZrO₂ and the (101) reflection for t-ZrO₂ using the following equations [40,41]:

\[ Xₘ = \frac{Iₘ(111) + Iₜ(111)}{Iₘ(111) + Iₜ(111) + Iₜ(101)} \quad (2) \]

and

\[ Vₘ = \frac{1.311Xₘ}{1 + 0.311Xₘ}. \quad (3) \]

This calculation cannot account for amorphous zirconia fractions, because they are not detectable by XRD.

2.2.4. Photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on the supported WO₃/ZrO₂ and WO₃/ZrO₂(OH)₄–₂ samples using a Phi Quantera spectrometer equipped with an aluminum anode (AlKα = 1486.6 eV) operated at 25 W (15 kV, 1.67 mA) with a 100-µm spot size and 3-kV ion gun accelerating voltage. The experiments were performed in a conventional ultrahigh-vacuum (UHV) chamber with a base operating pressure of typically ~7 × 10⁻⁶ N/m². Ambient-exposed, air-oxidized samples were compressed between two pieces of indium foil to minimize contamination, after which one of the powdered cake halves was mounted under a stainless steel bracket containing a 1-mm hole onto the sample platen. Equipment was not available to thermally dehydrate samples in situ within the XPS, so dehydration was achieved by holding at room temperature under UHV conditions. A minimum of 3 spots for each sample were simultaneously analyzed to test sample heterogeneity; the results reported here are averages of these multiple spots. A gold standard (binding energy, 84.2 eV) was used to verify instrument calibration. An Ulvac-Phi MultiPak nonlinear least squares curve-fitting program was used for data analysis with integral background.

2.2.5. Raman spectroscopy

Raman spectroscopy was used to obtain the molecular structures of the supported tungsten oxide catalysts with a visible (532 nm) laser excitation on 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, 150 mW; sample power, 10 mW) with the scattered photons directed into a single monochromator and focused onto a UV-sensitive liquid-N₂ cooled CCD detector (Horiba–Jobin Yvon CCD-3000V) with a spectral resolution of ~2 cm⁻¹ for the given parameters. The Raman spectrometer also was equipped with an environmentally controlled high-temperature environmental cell (Linkam, TS1500) that examined the catalyst samples in loose powder form (~5–10 mg) and also allowed for control of both the temperature and gaseous composition. In situ Raman spectra were collected for the supported tungsten oxide catalysts after dehydration at 723 K for 1 h in flowing 10% O₂/He (Airgas, certified, 9.735% O₂/He, UHP and hydrocarbon-free, 30 mL/min) to desorb the adsorbed moisture, and the spectra of the dehydrated samples were collected after the catalysts were cooled to 393 K in flowing 10% O₂/He gas to ensure that the catalyst surface was devoid of moisture. Spectral acquisition was done with 20 scans of 20 s/scan, for a total acquisition time of ~7 min per spectrum. System alignment was verified daily using a silica reference standard provided by Horiba–Jobin Yvon.

2.2.6. UV-vis diffuse reflectance spectroscopy

The electronic structures of the zirconia-supported tungsten oxide catalysts were obtained with a Varian Cary 5E UV-vis spectrophotometer using the integration sphere diffuse reflectance attachment (Harrick Praying Mantis Attachment, DRA-2). The finely ground powder catalyst samples (~20 mg) were loaded into an in situ cell (Harrick, HVC-DR2) and measured in the 200–800 nm region using a magnesium oxide reflectance standard as the baseline. The UV–vis spectra of the supported tungsten oxide catalysts were obtained after the samples were treated at 673 K for 1 h in flowing 10% O₂/He (Airgas, certified, 9.735% O₂/He, UHP and hydrocarbon-free, 30 mL/min) to desorb the adsorbed moisture. Time-resolved in situ methanol dehydration studies were also carried out with reactor feed compositions of 6:12:82% CH₃OH/O₂/He and 6:94% CH₃OH/He at a total flow of 50 mL/min to study the effect of reduced sites at a reaction temperature of 573 K. Be-
low 300 nm, the absorbance signal was unacceptably noisy, and thus a filter (Varian, 1.5 ABS) was used to minimize the background noise.

The UV–vis spectra were processed with Microsoft Excel software, consisting of the calculation of the Kubelka–Munk function, 

\[ F(R_{\infty}) = \frac{(1-R)^2}{2R} \]

which was extracted from the UV–vis DRS absorbance. The edge energy (\(E_g\)) for the allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of \([F(R_{\infty})h\nu]^n\), where \(n = 0.5\) for the direct allowed transition versus the incident photon energy, \(h\nu\) [42–44].

2.2.7. Transmission electron microscopy

Samples for bright field (BF) and high-resolution (HR) transmission electron microscopy (TEM) examination were prepared by grinding and dispersing the catalyst powder in high-purity ethanol, then allowing a drop of the suspension to evaporate on a lacy carbon film supported by a 300-mesh copper TEM grid. “Dry” samples also were prepared for comparative purposes by dipping the TEM grid into the dry catalyst powder and then shaking off any loosely bound residue. BF-TEM images of the samples after exposure to ambient conditions were obtained using a JEOL 2000FX device operating at 200 kV. HR-TEM images of the samples were obtained using a JEOL 22000FS instrument with an accelerating voltage of 200 kV, a point-to-point resolution of 0.19 nm, and an information limit of 0.11 nm. Chemical analyses by X-ray energy dispersive spectroscopy (XEDS) were carried out using a dedicated VG HB603 STEM equipped with a Nion aberration corrector.

2.3. Reactivity studies

2.3.1. Methanol temperature-programmed surface reaction spectroscopy

Methanol temperature-programmed surface reaction (TPSR) spectroscopy was performed on an Altamira Instruments AMI-200 temperature-programmed system linked by a capillary tube to an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS; Ametek Process Instruments). Typically, \(~100\ mg of catalyst was loaded in a U-type quartz tube and initially pretreated in flowing air at 723 K (Airgas, Ultra-Zero-Grade Air, 30 mL/min) for 40 min to remove any possible adsorbed organic impurities and to dehydrate the sample. To ensure that the surface WO\(_x\) species remained in a fully oxidized state, the pretreated samples were initially cooled to 383 K, at which point the gas stream was switched to helium (Airgas, UHP, 30 mL/min) to flush out any residual gas-phase O\(_2\). The sample was further cooled to 373 K and held for 30 min to remove any physically adsorbed O\(_2\) and background gases. At 373 K, methanol adsorption was performed by flowing 2000 ppm CH\(_3\)OH/He (Airgas, 30 mL/min) for 30 min, after which the system was purged with flowing helium (Airgas, UHP, 30 mL/min) for another 30 min to remove any residual physically adsorbed methanol. Afterward, the sample was heated at a constant heating rate (10 K/min) to 773 K in flowing helium (Airgas, UHP, 30 mL/min). The gases exiting from the quartz tube reactor were analyzed with the online mass spectrometer as a function of catalyst temperature. The following \(m/e\) ratios were used for the identification of the various desorption gases: CH\(_3\)OH, \(m/e = 31\); H\(_2\)CO, \(m/e = 30\); CH\(_3\)OCH\(_3\), \(m/e = 45\) and 15 (DME); CO, \(m/e = 28\); CO\(_2\), \(m/e = 44\); H\(_2\)O, \(m/e = 18\); H\(_2\)COOCH, \(m/e = 60\) (MF); and (CH\(_2\)O)\(_2\)CH\(_2\), \(m/e = 75\) (DMM). For those desorbing molecules that gave rise to several fragments in the mass spectrometer, additional \(m/e\) values also were collected to further confirm their identity. Recent studies demonstrated that the rate-determining step in methanol dehydration involves the first-order process that breaks the C–O bond in the surface CH\(_3\)O\(_x\) intermediate [45]. In addition, because the supported WO\(_x\)-zirconia samples are 100% acidic, forming only dimethyl ether (DME) as a product, the area under the DME/CH\(_3\)OH-TPSR curve corresponds to the number of exposed surface acid sites (\(N_s\)). By definition, \(N_s\) is equal to \(\rho_{W,\text{surf}}\) (W/nm\(^2\)) until monolayer coverage is reached, because the WO\(_x\) surface species are 100% dispersed in the sub-monolayer region. Above monolayer coverage, however, \(N_s\) was calculated from the following relationship:

\[
N_s = \frac{\text{ML}_{\text{DesorptionArea}} \times \text{AboveMLDesorptionArea}}{\text{MLDesorptionArea}}.
\]

2.3.2. Steady-state methanol dehydrogenation to dimethyl ether

Steady-state methanol dehydrogenation experiments were conducted in an ambient pressure reactor consisting of a single-pass downflow fixed-bed quartz reactor (0.167 ID) packed with finely ground catalyst powder and quartz endcaps. Catalyst loadings of 5–30 mg were chosen to maintain total methanol conversion under 10%, permitting the assumption of differential (i.e., gradientless) reactor conditions. To mimic thermal resistance and estimate catalyst bed temperature, a thermocouple mounted at the same elevation as the catalyst bed was installed inside an identical quartz tube that was fixed to the reactor tube. Both tubes were mounted side-by-side snugly within a 0.506 ID metal tube wrapped in heat tape and insulation. Pretreatment consisted of calcining each catalyst at 623 K for 30 min in a 94 mL/min dry flowing gas mixture of oxygen (UHP, Airgas) and helium (UHP, Airgas) controlled at a molar O\(_2\)-to-He ratio of 14:79 by two independent Coriolis mass flow controllers. The reactor was then cooled to 573 K, after which the feed gases were bubbled through a liquid methanol saturator (Alfa Aesar, ACS grade). The gas-phase methanol concentration was controlled by the temperature of an overhead condenser, operated at 281 K for these experiments. The final composition of the reactor feed stream was 6:12:82% CH\(_3\)OH/O\(_2\)/He at 100 mL/min total flow (ST = 273.15 K, 101,325 N/m\(^2\)). Steady-state performance was determined by averaging 3–4 gas chromatography (GC) cycles at 573 K, and comparing this value to those of the initial runs at 373 K, where each catalyst was consistently demonstrated to be inactive in converting methanol. Blank runs without the catalysts demonstrated negligible methanol conversion in the reactor system. The 0.250 OD stainless steel tubing from the reactor outlet to the GC was maintained at 393–423 K.
by heat tape and insulation, to minimize condensation of the reactor effluents. The reactor effluent gases were analyzed by an Hewlett Packard HP5890 Series II online gas chromatograph, operated in split mode (308 K for 6 min, ramp 20 K/min to 498 K hold for 5 min), with a 10-port Valco valve diverting two samples in parallel through a CP-sil 5CB capillary column (30 m × 0.32 mm × 5.0 μm; J&W Scientific) to a flame ionization detector and a 40/60 Carboxene-1000 packed column (5 ft × 1/8”, Supelco) to a thermal conductivity detector for determination of the methanol conversion, selectivity, and activity.

The steady-state methanol dehydration catalytic data are expressed in terms of turnover frequency (TOF; number of DME molecules formed/surface acid site/s) and turnover ratio (TOR; number of DME molecules formed/total W-atoms/s). For the supported tungsten oxide catalysts below monolayer coverage, the number of surface acid sites was taken to be the number of surface WO₃ species, which assumed 100% dispersion; this was independently confirmed with XPS and Raman spectroscopy. Above monolayer surface tungsten oxide coverage, the number of exposed surface acid sites was determined by the area under the DME/CH₃OH-TPSR curves and normalized to the value for monolayer coverage.

3. Result

3.1. Catalyst characterization

3.1.1. BET surface area

The BET surface area values for the supported WO₃/ZrO₂-(OH)₄₋ₓ catalysts as a function of WO₃ concentration and calcination temperature are given in Table 1. All of the trends observed with tungsten oxide loading and calcination temperature are consistent with those reported in the literature [20,25,46]. Increasing the calcination temperature at a constant WO₃ loading led to a continuous decrease in the BET surface area as the underlying amorphous zirconia support sinters, crystallizes, and undergoes significant pore collapse; however, the BET surface area went through a maximum as a function of WO₃ loading at a constant calcination temperature, which can be attributed to the surface stabilization of the ZrO₂ support by direct interaction with the surface WO₃ species. It is important to note that multiple samples with different WO₃ loadings and calcination temperatures can have similar ρₓ,Wsurf values for selected experimental conditions.

3.1.2. XRD

The XRD patterns for the WO₃-free zirconium oxyhydroxide support as a function of calcination temperature from 473 to 1173 K are shown in Fig. 1. The native ZrO₂(OH)₄₋ₓ support remained XRD-amorphous at calcination temperatures up to 573 K and crystallized to both the tetragonal-ZrO₂ (t-ZrO₂) and monoclinic-ZrO₂ (m-ZrO₂) polymorphs at higher temperatures. The volume fraction of t-ZrO₂ reached its maximum at 673 K, which is generally consistent with the previously reported behavior of hydrous zirconium oxide gels prepared at basic pH [47,48]. Higher calcination temperatures rapidly transformed the metastable t-ZrO₂ polymorph to the thermodynamically stable m-ZrO₂ polymorph. The t-ZrO₂ phase was almost completely transformed to the m-ZrO₂ polymorph at 1173 K.

The XRD patterns for all supported WZrOH catalysts also were consistent with previously reported trends [18,25,46]. For calcination temperatures ≥773 K, every sample had some fraction of t-ZrO₂, and most had at least a trace of m-ZrO₂. The volume fraction of the m-ZrO₂ phase in the supported WZrOH materials (balance t-ZrO₂) as a function of WO₃ content and calcination temperature is presented in Fig. 2. At the lowest calcination temperatures (773–873 K), m-ZrO₂ was not present in the catalyst samples with the highest WO₃ loading, due to the structure-stabilizing effect of highly dispersed surface tungstate species. The volume fraction of m-ZrO₂ increased with decreasing WO₃ loading at a constant temperature, providing further evidence of the stabilizing effect of surface WO₃. As would be expected based on thermodynamic considerations, increasing the calcination temperature at a constant WO₃ concentration increased the m-ZrO₂ volume fraction.

3.1.3. XPS

The XPS surface W/Zr atomic ratios of the model supported WZrO₂ and supported WZrOH catalytic systems are shown in Fig. 3 as functions of surface W-atoms/nm² density. For the model supported WZrO₂ catalyst system (represented by the solid curve), the surface W/Zr ratio is linear up to ρₓ,Wsurf ~ 4.5 W-atoms/nm² with an excellent least squares fit (R² = 0.994). Above 4.5 W-atoms/nm², the data points fall below the line, and the slope of the curve becomes very shallow due to the onset of crystalline WO₃ nanoparticles with diameters larger than the escape depth of excited electrons from the W(4f) transition (~2.63 nm) [49–51]; consequently, the W(4f)
Volume fraction of XRD-detectable crystalline ZrO$_2$ as m-ZrO$_2$ (balance t-ZrO$_2$) in WZrOH materials as a function of WO$_x$ surface loading and calcination temperature: 773 K (□), 873 K (○), 973 K (△), 1073 K (▽), 1173 K (◁).

Fig. 3. XPS surface W/Zr atomic ratios of vacuum dehydrated samples determined from area integration and sensitivity factor correction for W 4f$_{7/2}$ and Zr 3d$_{5/2}$. Sample series include “model” supported xWZrO$_2$-723 (■) and supported xWZrOH-773 (□), -873 (○), -973 (△), -1073 (▽), -1173 K (◁).

The XPS surface W/Zr atomic ratios for the supported WZrOH catalyst samples are also presented in Fig. 3 (open symbols) as a function of surface W-atoms/nm$^2$ density and calcination temperature. Qualitatively similar to the model supported WZrO$_2$ materials, the surface W/Zr ratio for each of the supported WZrOH series at constant calcination temperature increases linearly at low WO$_x$ loading, then exhibits a plateau or even a negative deviation at higher WO$_x$ concentrations. The negative deviation for the supported WZrOH materials at low and high tungsten oxide loadings suggests that the surface region also contains some extra ZrO$_2$ not present in the model supported WZrO$_2$ system. Assuming that the deviation from linearity for the WZrOH catalysts is due to WO$_3$ formation, the $\rho_{W,\text{surf}}$ at which the XPS W/Zr ratio deviates from linearity occurs at ~5 W-atoms/nm$^2$.

3.1.4. Raman spectroscopy
3.1.4.1. Zirconia support Raman spectroscopy provided unique molecular structural insights into both the amorphous and crystalline ZrO$_2$ phases. Although both crystalline t-ZrO$_2$ and m-ZrO$_2$ phases share strong overlapping bands at 476 and 637–647 cm$^{-1}$ [53,54], they also have additional unique vibrations at lower wavenumber values that allow discrimination between these two crystalline ZrO$_2$ phases. The m-ZrO$_2$ phase exhibits Raman bands at 180(s), 192(s), 220(w), 308(w), 335(m), 349(m), 383(m), 476(s), 539(w), 561(w), 617(m), 638(m), and 756(w) cm$^{-1}$, whereas the Raman spectrum of the t-ZrO$_2$ phase contains bands at 149(m), 263–272(s), 290(w), 319(m), 412–423(w), 464(m), 476(s), 577(w), and 647(w) cm$^{-1}$ [25,53,54].

The Raman spectra for WO$_x$-free zirconium oxyhydroxide as a function of calcination temperature, depicted in Fig. 4, are consistent with the XRD findings. The Raman bands for the 573–673 K calcined samples are very broad and characteristic of mostly amorphous materials; however, characteristic Raman vibrations due to crystalline t-ZrO$_2$ and m-ZrO$_2$, which cannot be detected by XRD, are also present. The highest concentrations of t-ZrO$_2$ are found at 573–673 K, and at increasing calcination temperature, loss of the Raman band at $\sim$153 cm$^{-1}$ reflects progress of the phase transformation of t-ZrO$_2$ to m-ZrO$_2$ through the growth of the doublet at $\sim$179 and $\sim$208 cm$^{-1}$ in
Fig. 5. Raman spectra (532 nm) under dehydrated conditions as a function of calcination temperature (K) and surface tungsten oxide coverage (W-atoms/nm²) of supported tungsten oxide on the ZrOₓ(OH)₄⁻²ₓ support: (A) CT 773 K, (B) CT 873 K, (C) CT 973 K, (D) CT 1073 K, and (E) CT 1173 K.

The Raman spectra, as well as the strong and medium bands at \(\sim 325\) and \(\sim 367\) cm\(^{-1}\), respectively.

3.1.4.2. Supported WO₃/ZrO₄(OH)₄⁻₂ₓ catalysts The Raman spectra of the supported WO₃/ZrO₄(OH)₄⁻₂ₓ catalysts under dehydrated conditions are shown in Fig. 5. The supported WO₃/ZrO₄(OH)₄⁻₂ₓ Raman spectra do not contain the features of crystalline Zr(WO₄)₂ [Raman features at 1028(s), 968(m), 931(s), 904(s), 860(m), 790(s), 734(s), 473(w), 378(s), 330(s), 305(m), 231(m), 175(w), 187(w), and 138(s) cm\(^{-1}\)] [55].
Keggin $[XW_{12}O_{40}]^{3-}$ heteropolyacids [Raman features at 950–1015 cm$^{-1}$ ($v_s(W=O)$), 825–930 cm$^{-1}$ ($v_a(W=O)$), ~504–734 cm$^{-1}$ (bridging $W-O-W$), and 149–450 cm$^{-1}$ ($\delta(W-O-W)$)] [58]. Wells–Dawson $a_1[X_2W_{18}O_{62}]^{9-}$ heteropoly anions, and Wells–Dawson $a_2-[X_2W_{17}O_{61}]^{10-}$ lacunary species [multiple Raman $W=O$ vibrations between 950–1005 cm$^{-1}$ reflecting a distribution of distortions among the $WO_6$ units in the framework, as well as vibrations at ~500–700 cm$^{-1}$ (bridging $W-O-W$) and 129–380 cm$^{-1}$ ($\delta(W-O-W)$)] [55]. But the Raman features of crystalline $m$-WO$_3$ (133(s), 178(w), 187(w), 272(s), 327(m), 417(w), 437(w), 448(w), 715(s), and 805(s) cm$^{-1}$) [59–62] are present for high tungsten oxide $\rho_{\text{surf}}$ values and high calcination temperatures. The Raman spectra of the tungsten oxide component are generally found in the 700–1200 cm$^{-1}$ region, because the strong crystalline ZrO$_2$ support vibrations tend to dominate the spectra below 700 cm$^{-1}$ [31,36].

The Raman spectra in the 100–700 cm$^{-1}$ region of Fig. 5 reveal that the crystallization of the zirconia support is strongly affected by both the supported tungsten oxide phase and the calcination temperature. At low $\rho_{\text{W,surf}}$ values, the zirconia support gives rise to well-defined $m$-ZrO$_2$ Raman bands. As the $\rho_{\text{W,surf}}$ value increases, the zirconia Raman bands broaden, reflecting the presence of smaller crystallites or less-ordered ZrO$_2$ particles, due to the retardation of zirconia crystallization by the supported tungsten oxide phase. At the highest $\rho_{\text{W,surf}}$ and modest calcination temperatures, the zirconia support Raman features are extremely weak and broad, reflecting the presence of an amorphous zirconia phase. Comparing the Raman spectra of W-free ZrO$_2$ and supported WO$_3/ZrO_2$ (OH)$_4$–$2x$ shown in Figs. 4 and 5, respectively, at the same calcination temperature further emphasizes the retarding influence of the supported tungsten oxide phase on the crystallization of the ZrO$_2$ phase. Increasing the calcination temperature accelerates the crystallization of the zirconia support and tends to give rise to sharper ZrO$_2$ bands.

The Raman spectra in Fig. 5 also contain molecular structural information about the supported tungsten oxide phase in the 700–1200 cm$^{-1}$ region. All of the dehydrated supported WZrOH catalyst samples exhibit a Raman band at ~1001–1020 cm$^{-1}$ (bridging $W-O-W$) and 129–380 cm$^{-1}$ ($\delta(W-O-W)$), as we elaborate on below.

3.1.4.3. Amorphous WO$_3$ phases The major difference between the Raman spectra of the supported WZrOH and the model supported WZrO$_2$ catalytic materials is the presence of the broad bands in the ~820–850 cm$^{-1}$ and ~900–925 cm$^{-1}$ regions for the supported WZrOH system, as shown in Fig. 6 [37,38]. The very broad nature of these Raman bands suggests that they may be associated with poorly ordered NPs. To investigate this possibility, the crystallization of amorphous WO$_3$ in the presence and absence of a minor amount of ZrO$_2$ (OH)$_4$–$2x$ was examined. Amorphous WO$_3$ readily undergoes crystallization to well-ordered WO$_3$ with sharp Raman bands at relatively mild calcination temperatures (~673 K), as shown in Fig. 7A. Interestingly, weak vibrations in the 970–1020 cm$^{-1}$ region are also present in the Raman spectra from some surface WO$_3$ species on this bulk tungsten oxide material with a relatively higher surface area. The addition of a small amount of ZrO$_2$ (OH)$_4$–$2x$, by aqueous impregnation onto the initial amorphous WO$_3$ material, dramatically retards the crystallization of the amorphous WO$_3$ phase, as shown in Fig. 7B. Even at very high calcination temperatures, the sharp characteristic Raman bands of crystalline WO$_3$ are still absent. An additional feature present in the ZrO$_2$ (OH)$_4$–$2x$/WO$_3$ sample not found in the Zr-free WO$_3$ sample is a strong broad band in the 915–950 cm$^{-1}$ region. Raman bands in the 915–950 cm$^{-1}$ region are associated with bridging MO$_x$–O–Zr bonds [73], and such a weak band also has been detected for the model supported WO$_3$ catalysts [37,38]. Although the broad Raman bands in the 820–850 cm$^{-1}$ region are not present for the calcined ZrO$_2$/WO$_3$/WO$_3$ sample, keep in mind that this sample consists of large tungsten oxide domains, whereas the supported WZrOH catalysts contain only small crystalline WO$_3$ particles. The slight shift of the crystalline WO$_3$ band from 805 cm$^{-1}$ to ~820–850 cm$^{-1}$, along with the shift of this latter band from...
3.1.5.1. Dehydrated conditions

The UV–vis DRS spectra of initially amorphous WO₃ and 10% ZrO₂–WO₃ mixture as a function of calcination temperature.

The bands at ~820–850 cm⁻¹ arise from distorted or poorly ordered WO₃ NPs that become more or less of calcination temperature. Thus, the additional bands present in the Raman spectra of the supported WZrOH catalysts at ~820–850 and 900–925 cm⁻¹ are related to Zr-stabilized distorted WO₃ NPs (Zr-WO₃).

3.1.4.4. Raman summary

In summary, four different tungsten oxide structures were found to be present in supported WZrOH catalysts under dehydrated conditions: isolated surface mono-oxo W=O species (~1000 cm⁻¹), polymeric surface mono-oxo W=O species (~1020 cm⁻¹), distorted Zr-WO₃ NPs (~820–850 cm⁻¹ and ~900–925 cm⁻¹), and well-ordered crystalline WO₃ NPs (~805, ~715, and ~270 cm⁻¹).

3.1.5. UV–vis DRS

3.1.5.1. Dehydrated conditions

The UV–vis DRS $E_g$ values for the dehydrated supported WO₃/ZrO₂(OH)₄−2x (open symbols) and the model supported WO₃/ZrO₂ (closed symbols) catalyst systems are presented in Fig. 8 as a function of $\rho_{W,\text{surf}}$ and calcination temperature. For the well-defined model supported WZrO₂ samples in the sub-monolayer region (<4.5 W-atoms/nm²), the $E_g$ value drops from 5.2 to 4.2 eV with increasing surface tungsten oxide coverage. The corresponding ligand-to-metal charge transfer (LMCT) band maxima are observed at 218–219 and 240–246 nm, with a shoulder at 250–268 nm [55]. The $E_g$ values and corresponding LMCT transitions of bulk tungstate reference compounds indicate that this value of 5.2 eV corresponds to monotungstate WO₃ structures, and the value of 4.2 eV corresponds to a mixture of monotungstate and polytungstate WO₃ structures [55]. The decrease in $E_g$ values with increasing $\rho_{W,\text{surf}}$ up to monolayer coverage (4.5 W/atm²) in the model supported WZrO₂ system reflects the fact that the surface WO₃ species are becoming polymerized, with the extent of polymerization increasing very rapidly in the low-$\rho_{W,\text{surf}}$ region [58]. In the second region, between 4.5 and 10 W-atoms/nm², the $E_g$ value continues to decrease with increasing tungsten oxide loading from 4.2 to 3.8 eV due to the presence of crystalline WO₃ NPs above monolayer coverage (see the Raman spectra in Fig. 6) [37,38]. Above 10 W-atoms/nm², the $E_g$ value remains relatively constant with increasing $\rho_{W,\text{surf}}$, because large crystalline WO₃ particles are present, and the $E_g$ value effectively approaches that of bulk WO₃ crystals.

The UV–vis DRS $E_g$ values for the supported WZrOH series track the same $E_g$ value trend of the model supported WZrO₂ series in the sub-monolayer region up to ~4.5 W/nm² regardless of calcination temperature. The corresponding LMCT band maxima occurs at ~250 nm for all of the supported WZrOH catalysts, which is characteristic of highly distorted monotungstate and polytungstate WO₃ structures [55]. An additional LMCT band at ~230 nm from regular monotungstate WO₃ species [55] is observed only for the 5.1WZrOH-873(2.6), 10.1WZrOH-873(3.9), and 5.1WZrOH-1173(5.9) catalyst samples. This decreasing trend in $E_g$ value at low $\rho_{W,\text{surf}}$ values reflects the enhanced electron delocalization with increasing domain size of surface WO₃ species in going from isolated to polymeric structures. The overlapping $E_g$ values for the two catalyst series suggests that the electronic structure of the surface WO₃ species is generally similar for both supported WZrOH and WZrO₂ catalyst systems in this region. For higher $\rho_{W,\text{surf}}$, the $E_g$ value for the supported WZrOH series further decreases from ~4.2 to 4.0 eV until ~10 W-atoms/nm² is attained and then remains constant at this value for all high surface W-atoms/nm² density. The further decrease in $E_g$ value from ~5–10 W-atoms/nm² reflects the presence of WO₃ 3D nanodomains (as confirmed by the Raman spectra in Fig. 5). A striking difference between the supported WZrOH and WZrO₂ series is the slightly higher $E_g$ values for the WZrOH system above ~4.5 W-atoms/nm². This higher
$E_g$ value for the supported WZrOH catalysts is attributed to the presence of the smaller Zr-stabilized distorted WO3 NPs (Zr-WO3) that are not present in the model WZrO2 catalysts. Furthermore, the constant $E_g$ value of $\sim$4.0 eV above $\sim$10 W-atoms/nm$^2$ reflects the fact that large bulk-like WO3 crystallites are not present for the supported WZrOH system, in direct contrast to the supported WZrO2 system in this $\rho_{W, \text{surf}}$ region.

### 3.1.5.2. Reaction conditions

The time-resolved in situ UV–vis DRS spectra of the very active supported 15WZrOH-973(6.2) catalyst (see Section 3.2.2 below) under different reaction conditions at 573 K are presented in Fig. 9. UV–vis DRS can follow the oxygen LMCT bands for both the W 6+ species at monolayer coverage; (iii) well-ordered WO3 and distorted Zr-WO3 NPs above monolayer coverage for WZrO2 and WZrOH, respectively; and (iv) bulk-like crystalline WO3 particles and Zr-stabilized WO3 NPs above $\sim$10 W-atoms/nm$^2$ for WZrOH. The distorted Zr-WO3 NPs present for WZrOH catalysts consist of smaller domains than the well-ordered WO3 NPs. Furthermore, reduced W$^{5+}$ cations also are present under the reducing conditions of CH3OH/He, and their presence is not related to DME formation.

#### 3.1.5.3. UV–vis DRS summary

In summary, the UV–vis DRS measurements reflect the presence of four distinct tungsten oxide structures in the supported WZrOH and WZrO2 catalytic materials under dehydrated conditions: (i) isolated surface WO$_x$ species at very low surface coverage; (ii) polymeric surface WO$_x$ species at monolayer coverage; (iii) well-ordered WO3 and distorted Zr-WO3 NPs above monolayer coverage for WZrO2 and WZrOH, respectively; and (iv) bulk-like crystalline WO3 particles and Zr-stabilized WO3 NPs above $\sim$10 W-atoms/nm$^2$ for WZrOH.
Fig. 10. Representative bright field (BF) images of supported tungsten oxide on the initial ZrO$_x$(OH)$_{4-2x}$ support: (A) W-free ZrO$_x$(OH)$_{4-2x}$-773, (B) 10.1WZrOH-773(2.9), (C) 19.5WZrOH-873(5.5), (D) 23.3WZrOH-973(9.5), (E) 10.1WZrOH-1073(6.2), and (F) 19.5WZrOH-1173(20.2).

773. The smaller ZrO$_2$ particles present in WZrOH-773 are a direct consequence of the strong interaction between the WO$_x$ species and the ZrO$_x$(OH)$_{4-2x}$ support during its crystallization. Internal voids within support grains were not found for the model supported WZrO$_2$ catalyst system, which consists of dense, coarse m-ZrO$_2$ particles with only some retained intergranular porosity [39].

3.1.6.2. Supported tungsten oxide domains

The BF images in Figs. 10B–10F also contain ~1-nm dark flecks that STEM-XEDS elemental analysis revealed to be rich in tungsten. These WO$_x$-containing domains are occasionally observed, especially by annular dark-field imaging, even at a very low $\rho_{W,\text{surf}} = 2.9$ W-atoms/nm$^2$ for the 10.1WZrOH-773(2.9) catalyst sample in which crystalline WO$_3$ is not present (according to the corresponding Raman spectra in Fig. 5). Similarly, these features also are found in the supported 19.5WZrOH-873(5.5) and 10.1WZrOH-1073(6.2) catalysts (Figs. 10C and 10E, respectively), in which crystalline WO$_3$ is not detected with Raman spectroscopy.

Representative HR-TEM images of the supported WZrOH catalysts are shown in Fig. 11 for selected supported WZrOH catalysts. The amorphous overlayer of surface WO$_x$ species is visible when viewed in profile, with the small WO$_x$-rich domains observed in Figs. 11B–11E as darker flecks against the zirconia support due to their higher mass contrast. A general trend of increasing number density of the dark WO$_x$-rich specks with increasing W-atoms/nm$^2$ is seen. The smallest number density of WO$_x$-rich domains is present at the lowest calcination temperatures and $\rho_{W,\text{surf}}$, and the largest number density WO$_x$-rich domains is present at the higher calcination temperatures and $\rho_{W,\text{surf}}$. A gradual slight increase in the average fleck dimensions, irrespective of whether the TEM samples were prepared by the wet or dry route, also was noted in this particular series of samples (i.e. 873 K samples: 0.6–0.8 nm; 973 K samples: 0.8–0.9 nm; 1073 K samples: 0.7–1.1 nm; 1173 K samples: 1.0–1.3 nm). At low $\rho_{W,\text{surf}}$ values (<6 W-atoms/nm$^2$), the tungsten-rich domains most likely correspond to hydrated WO$_x$ clusters (e.g., H$_6$W$_6$O$_{21}\cdot n$H$_2$O) [56] and possibly Zr-stabilized distorted WO$_3$ NPs that were de-
ected with Raman spectroscopy, because the signature resonances for well-ordered crystalline WO$_3$ particles are absent in the Raman spectra. At high $\rho_{\text{W},\text{surf}}$ values ($> 6$ W-atoms/nm$^2$), the tungsten-rich flecks most likely correspond to distorted Zr-WO$_3$ NPs and hydrated WO$_3$ clusters. Corresponding SEM images revealed that large (2–6 µm) WO$_3$ crystals also are present in samples at $\sim 8$ W/nm$^2$ and higher surface tungsten oxide density values.

3.2. Reactivity studies

3.2.1. Methanol-TPSR and $N_\ell$ determination

Methanol-TPSR dehydration studies were conducted to chemically probe the nature of the catalytic active sites present in the zirconia-supported tungsten oxide catalysts, because this reaction is known to proceed readily over surface acidic sites [59]. Unfortunately, the methanol dehydration reaction does not discriminate between Lewis and Brønsted acid sites, but does provide quantitative information about the number of exposed surface WO$_3$ catalytic active sites, $N_\ell$, which is reflected in the area under the DME-TPSR product curve.

The determined $N_\ell$ values are plotted in Fig. 12 for the supported WZrOH catalysts (open symbols) and compared with those of the model supported WZrO$_2$ catalysts (solid curve and closed symbols) as a function of $\rho_{\text{W},\text{surf}}$. Measurements were not made below 4.5 W-atoms/nm$^2$, because exposed ZrO$_x$ sites also are present in this region (dashed linear region). The linear increase in $N_\ell$ from 0 to 4.5 W-atoms/nm$^2$ was simply taken from the number of W atoms in the catalyst, because, by definition, the surface WO$_3$ species are 100% dispersed in the sub-monolayer region. Depending on calcination temperature and WO$_3$ loading, either a gentle increase or decrease in $N_\ell$ is observed in the 4.5–10 W-atoms/nm$^2$ range, with a significant decrease above 10 W-atoms/nm$^2$ for both the supported WZrOH and WZrO$_2$ catalyst series. The decrease in $N_\ell$ above 10 W-atoms/nm$^2$ reflects the presence of less-dispersed and larger WO$_3$ crystallites that have fewer exposed sites than the dispersed surface WO$_3$ phase. Compared with the model supported WZrO$_2$ series, the supported WZrOH catalysts at higher calcination temperatures typically have higher $N_\ell$ values, suggesting that a slightly greater number of catalytic active sites may be present for the supported WZrOH series than for the supported WZrO$_2$ series.

3.2.2. Steady-state methanol dehydration

Steady-state methanol dehydration studies were conducted to examine the surface acidic properties of the supported WZrOH catalysts. Every catalyst sample yielded 100% selectivity to dimethyl ether (DME), verifying the acidic nature of the supported WZrOH catalysts. Multiple samples were tested in both the presence and absence of a gaseous oxygen co-feed, and no appreciable difference in catalytic activity was observed when gaseous molecular O$_2$ was present or absent in the feed. This demonstrates that (i) the reaction is zero-order with respect to oxygen, (ii) a redox surface reaction mechanism does not occur, and (iii) partially reduced WO$_3$ species are not the acidic catalytically active site for methanol dehydration under the test conditions (consistent with the UV–vis DRS measurements reported above). Consequently, the catalytic data presented in Fig. 13 were obtained with oxygen-containing feed streams.

3.2.2.1. Catalytic TOF results

The catalytic TOF values for the supported WZrOH and WZrO$_2$ systems are plotted in Fig. 13A as a function of $\rho_{\text{W},\text{surf}}$. The reaction rates were converted to TOF values using the $N_\ell$ values determined from the CH$_3$OH-TPSR experiments and are shown in Fig. 13A. The resulting TOF curves for the model supported WZrO$_2$ and the supported WZrOH series differ significantly at the same $\rho_{\text{W},\text{surf}}$ value, indicating that factors other than surface W-atoms/nm$^2$ significantly affect the TOF value. The TOF for the supported WZrOH catalysts increases monotonically to $\rho_{\text{W},\text{surf}} \sim 6$ W-atoms/nm$^2$, then decreases with further increases in $\rho_{\text{W},\text{surf}}$. The supported WZrOH catalysts calcined at 773 and 1173 K do not attain TOF values comparable to those of the supported WZrOH samples calcined at 873–1073 K and are an order of magnitude less active than the highest TOF achieved. But the supported WZrOH catalysts calcined at 773 and 1173 K still exhibit TOF values that are a factor of $10^1$–$10^2$ greater than the those of the model supported WZrO$_2$ catalysts. Another interesting difference between the supported WZrOH and the model supported WZrO$_2$ catalyst system is that the TOF for the former system decreases above $\rho_{\text{W},\text{surf}} \sim 6$ W-atoms/nm$^2$, whereas that for the latter continues to increase with increasing $\rho_{\text{W},\text{surf}}$ above this level.

3.2.2.2. Catalytic TOR results

The catalytic TOR values, presented in Fig. 13B, were determined by normalizing the catalytic activity by all of the W atoms in the catalyst whether present as surface WO$_3$ species or as crystalline WO$_3$ NPs, with the latter clearly having dispersion significantly <100%. This overcounting of catalytically active sites decreases the TOR values at high $\rho_{\text{W},\text{surf}}$ values and contributes to the maximum

Fig. 12. Number of exposed W-sites/nm$^2$ for zirconia-supported tungsten oxide catalysts as a function of surface density (W-atoms/nm$^2$) for “model” xWZrO$_2$-723 (■) and xWZrOH-773 (○), -873 (△), -973 (△, -1073 (▲)), -1173 (◆).
in TOR at intermediate $\rho_{W,\text{surf}}$ values. For example, the TOF plot for the model supported WZrO$_2$ series does not exhibit a maximum, but does have a maximum at $\sim$8 W-atoms/nm$^2$ when plotted as TOR. For the supported WZrOH series, the TOF maximum occurs at $\sim$6 and at $\sim$8 W-atoms/nm$^2$ for TOR. Thus, the maximum in TOR plots is an artificial maximum that is a consequence of overcounting the number of catalytically active sites. Nevertheless, the current acid-catalyzed CH$_3$OH dehydration studies corroborate previous studies using $n$-butanol dehydration, $n$-pentane isomerization, $n$-heptane isomerization, and $o$-xylene isomerization indicating that the acid catalysis for supported WO$_x$–ZrO$_2$ materials exhibits TOR maxima at intermediate $\rho_{W,\text{surf}}$ values [17–19,21,23]. In addition, the TOR values for the supported WZrOH series is about a factor of 10$^2$ greater than the TOR values for the model supported WZrO$_2$ series, which is in agreement with early observations by Hino and Arata [1].

4. Discussion

4.1. Zirconia support

The W-free zirconium oxyhydroxide amorphous material is metastable and readily crystallizes to t-ZrO$_2$ and m-ZrO$_2$ phases at 673 K and above, with the thermodynamically more stable crystalline m-ZrO$_2$ phase dominating at higher temperatures. But the supported WZrOH catalyst system tends to crystallize as mixtures of t-ZrO$_2$ and m-ZrO$_2$. The t-ZrO$_2$ phase dominates for high $\rho_{W,\text{surf}}$ and more modest calcination temperatures (773–1073 K), whereas the m-ZrO$_2$ phase dominates for low $\rho_{W,\text{surf}}$ and especially high calcination temperatures. The morphology of the ZrO$_2$ particles also is affected by the presence of WO$_x$ and results in smaller ZrO$_2$ crystallites with a higher BET surface area. The stabilization of the t-ZrO$_2$ phase and the formation of smaller ZrO$_2$ particles for the WZrOH catalyst samples are a direct consequence of the interaction of WO$_x$ with the ZrOH substrate during its crystallization to ZrO$_2$.

The possible relationship between methanol dehydration catalytic activity of the supported WZrOH catalysts and the ZrO$_2$ crystalline phase composition is examined in Fig. 14, which plots the TOF against the m-ZrO$_2$ volume fraction, as determined from XRD measurements. For a wide range of m-ZrO$_2$ volume fractions, essentially the same TOF value is observed, suggesting that the specific ZrO$_2$ crystalline phase does not significantly affect the catalytic activity.
not affect the TOF for methanol dehydration to DME over the supported WZrOH catalysts [60,61]. The metastable ZrO$_2$($\text{OH})_{4-x}$ support also affects the crystallization of the initially amorphous WO$_x$ component, because Zr-stabilized distorted WO$_3$ NPs are formed both below and above monolayer coverage (see Figs. 5 and 6). The distorted Zr-WO$_3$ NPs are not present when crystalline m-ZrO$_2$ is used as a support and are present only when metastable ZrO$_2$($\text{OH})_{4-x}$ is used as the support. Thus, some of the metastable ZrO$_2$($\text{OH})_{4-x}$ component is able to interact and intermix with the amorphous WO$_x$ component during the crystallization process (see Fig. 7).

### 4.2. Monolayer surface WO$_x$ coverage

Monolayer surface coverage for the supported WZrOH catalyst system deviates slightly from the strict definition of monolayer coverage, because some Zr-stabilized distorted WO$_3$ NPs also are present below monolayer coverage (see the Raman spectra in Figs. 5 and 6). Despite this minor difference, however, the XPS surface analysis of the supported WZrOH and model supported WZrO$_2$ catalysts demonstrate that comparable monolayer coverage of $\rho_{\text{W,surf}} \sim 4.5–5$ W-atoms/nm$^2$ is obtained for both catalytic systems regardless of the crystallographic form of the underlying support material (i.e., t-ZrO$_2$, m-ZrO$_2$, or their mixtures). For the supported WZrOH catalyst series, the XPS W/Zr ratios are slightly below those of the model supported WZrO$_2$ series, suggesting enrichment of Zr in the surface region at the low and high $\rho_{\text{W,surf}}$ values. Such Zr enrichment can result from smaller WO$_3$ NPs, especially the presence of smaller Zr-stabilized WO$_3$ NPs.

The experimental data reported for monolayer coverage of surface WO$_x$ species is actually consistent among investigators. Previous XPS, ISS, CO-chemisorption, and Raman spectroscopy characterization of supported WZrO$_2$ by Vaidyanathan et al. [36,49] concluded that monolayer coverage of WO$_x$ species corresponds to $\rho_{\text{W,surf}} \sim 4$ W-atoms/nm$^2$, and that crystalline WO$_3$ NPs also are present at higher $\rho_{\text{W,surf}}$ values. Using low-temperature IR spectroscopy with CO-chemisorption and tracing the disappearance of the surface Zr–OH vibrations and the effect of CO on the vibrations of the W=O stretching modes, Scheithauer et al. [17] also concluded that monolayer surface coverage for supported WZrOH corresponds to $\rho_{\text{W,surf}} \sim 4.0–4.8$ W-atoms/nm$^2$. Using Raman spectroscopy, Barton et al. [22] similarly found that the $\sim 805$ cm$^{-1}$ band for crystalline WO$_3$ NPs was absent for the catalyst samples with $\rho_{\text{W,surf}} < 5$ W/nm$^2$ but present at higher loadings and increased linearly with loading $>5$ W-atoms/nm$^2$. From CO$_2$-chemisorption in which the surface Zr–OH groups were titrated, Barton et al. also found that all the exposed surface Zr–OH exposed by titration for the WO$_3$ species when $\rho_{\text{W,surf}}$ approached $\sim 4.5$ W-atoms/nm$^2$, which is consistent with monolayer coverage reported previously [22]. A similar chemical transition also was observed at $\rho_{\text{W,surf}} \sim 4.1$ W-atoms/nm$^2$ during H$_2$ reduction monitored by UV–vis [22]. The supported WO$_3$ species on ZrO$_2$ was not reduced at $<4.1$ W-atoms/nm$^2$ but was reduced at $>4.1$ W-atoms/nm$^2$. It was proposed that the only the samples at $>4.1$ W/nm$^2$ contained the W–O–W bonds needed to reduce the surface polytungstate and crystalline WO$_3$ domains [22]. The present study demonstrates that surface polytungstate species, with bridging W–O–Zr bonds, are present at $<4.5$ W-atoms/nm$^2$, and that crystalline WO$_3$ and distorted Zr-WO$_3$ NPs, primarily containing bridging W–O–W bonds, become dominant above monolayer coverage ($>4.5$ W-atoms/nm$^2$). Therefore, all of the experimental characterization studies reported the past three decades indicate that monolayer surface coverage for supported tungsten oxide catalysts on ZrO$_2$ corresponds to $\rho_{\text{W,surf}} \sim 4–5$ W-atoms/nm$^2$ and is independent of the type of oxide support (with the exception of inert SiO$_2$ support) [17,20,22,25,36,49,57,62–72].

The only differing monolayer surface WO$_x$ coverage values reported in the literature correspond to theoretical estimates that are based on bulk structural assumptions of how a crystalline WO$_3$ lattice hypothetically would interact with the relatively perfect surface of crystalline ZrO$_2$. As is well known, and has been strikingly demonstrated above, the supported tungsten oxide phase and the ZrO$_2$ support structures cannot be represented by model crystalline WO$_3$ and crystalline ZrO$_2$ phases, respectively.

### 4.3. Nature of WO$_x$ species in the sub-monolayer region (<5 W-atoms/nm$^2$)

The combined in situ UV–vis and Raman studies of the supported WZrOH catalysts indicate that the dehydrated surface WO$_3$ species become progressively polymerized with surface tungsten oxide coverage in the sub-monolayer region. This is reflected by the decrease in the UV–vis $E_g$ value from $\sim 4.5$ to $\sim 4.0$ eV due to polymerization of the surface WO$_x$ species and the shift of the W=O Raman band from $\sim 1000$ to $\sim 1020$ cm$^{-1}$, corresponding to monotungstate and polytungstate surface $\text{O}_x\text{W}=\text{O}$ species, respectively [55]. The same dehydrated surface WO$_x$ species as a function of surface coverage in the sub-monolayer region also are present for the model supported WZrO$_2$ catalysts, because both the UV–vis $E_g$ values and Raman band positions vary in a similar manner as a function of $\rho_{\text{W,surf}}$ for both the supported WZrOH and supported WZrO$_2$ series up to monolayer coverage (see Figs. 5–7) [37,38].

There is only one significant difference between the supported WZrOH and model WZrO$_2$ catalyst series in the sub-monolayer region. The supported WZrOH catalysts also have some Zr-stabilized distorted WO$_3$ NPs (see the Raman spectra in Figs. 5 and 6). But the concentration of these distorted Zr-WO$_3$ clusters in the sub-monolayer region cannot be high, because the overall UV–vis $E_g$ values are not significantly perturbed by their presence (compare the behavior of WZrOH and WZrO$_2$ in Fig. 8). Raman bands at $\sim 820$ and $910–950$ cm$^{-1}$ corresponding to distorted Zr-WO$_3$ NPs also have been reported by Barton et al. and Knozinger et al. in the monolayer region [17,22,25]. The former group did not discuss these Raman bands; the latter group assigned them to possible Zr-WO$_3$ heteropoly anions (HPAs), based on low-temperature CO chemisorption evidence of exposed Zr at high tungsten ox-
Three-dimensional WO$_3$ NPs above monolayer coverage for talline WO$_3$ NPs coexist with the distorted Zr-WO$_3$ NPs, as dramatically, to $\rho$ supported WZrO$_2$ catalyst series does not represent the catalytic active sites, because its TOF for the supported WZrO$_2$ series is a factor of $\sim 10^1$–$10^2$ lower than that of the monolayer-covered supported WZrOH catalyst, which also contains some Zr-stabilized distorted WO$_3$ NPs (see Fig. 13). The supported WZrOH catalyst with the highest TOF corresponds to $\rho_{W,\text{surf}} \sim 6$ W-atoms/nm$^2$, just above monolayer coverage, where crystalline WO$_3$ NPs are expected. The corresponding Raman spectra reveal that generally, only Zr-stabilized WO$_3$ NPs are present for all of the supported WZrOH catalyst samples at $\rho_{W,\text{surf}} \leq 7$ W-atoms/nm$^2$. The lower TOF/TOR activity of the supported WZrOH catalysts with $\rho_{W,\text{surf}} > 9$ W-atoms/nm$^2$ is associated with the presence of bulk-like crystalline WO$_3$ particles, which have only modest acidic activity, and probably are also covering up some of the more active catalytic surface sites (see Fig. 13). The supported WZrOH catalysts are still significantly more active than the model supported WZrO$_2$ catalysts for $\rho_{W,\text{surf}} > 9$ W-atoms/nm$^2$ because of the presence of some distorted Zr-WO$_3$ NPs that are not present in the model supported WZrO$_2$ catalyst system. This also is demonstrated in further studies in which introduction of Zr-WO$_3$ NPs into the model WZrO$_2$ catalyst was found to increase the TOF by as much as a factor of $10^2$.

Previous studies with similar supported WZrOH catalysts have proposed that the acidic catalytic activity of supported WZrOH catalysts for $o$-xylene isomerization and 2-butanol dehydration is only a function $\rho_{W,\text{surf}}$ and corresponds to a two-dimensional surface polytungstate monolayer present in a partially reduced state [18–22,25–29,31]. However, the most active and least active TOFs for supported WZrOH catalysts for methanol dehydration, have the same $\rho_{W,\text{surf}}$ values at $\sim 6$ W-

### 4.4. Nature of WO$_x$ species above monolayer coverage

The two-dimensional surface WO$_x$ monolayer coexists with three-dimensional WO$_3$ NPs above monolayer coverage for both the supported WZrOH and model WZrO$_2$ catalyst series. For the model supported WZrO$_2$ catalysts, the WO$_3$ NPs are present only as well-ordered WO$_3$ crystallites. For the supported WZrOH catalysts just above monolayer (5–8 W-atoms/nm$^2$), however, the WO$_3$ NPs are generally present as Zr-stabilized distorted WO$_3$ NPs at modest calcination temperatures. At higher $\rho_{W,\text{surf}}$ and calcination temperatures, well-ordered crystalline WO$_3$ NPs coexist with the distorted Zr-WO$_3$ NPs, as indicated by the higher UV–vis $E_\gamma$ values for the supported WZrOH series compared with those for the model supported WZrO$_2$ series (see Fig. 8).

### 4.5. Determination of catalytic active sites for supported WZrOH catalysts

The only substantial difference between the model supported WZrO$_2$ and WZrOH catalysts in the sub-monolayer region is the presence of the Zr-stabilized distorted WO$_3$ NPs for the supported WZrOH catalysts, as depicted in Scheme 1 (see Fig. 6). Thus, the enhancement of acidic TOF/TOR activity by a factor of $10^1$–$10^2$ for the supported WZrOH catalysts must be due to the presence of the distorted Zr-WO$_3$ NPs, because this is the only different tungsten oxide component between the supported WZrOH and WZrO$_2$ catalyst series. Importantly, this also demonstrates that a monolayer of surface polytungstate species on ZrO$_2$ which is present for the model supported WZrO$_2$ catalyst series does not represent the catalytic active sites, because its TOF for the supported WZrO$_2$ catalyst series is a factor of $\sim 10^1$–$10^2$ lower than that of the monolayer-covered supported WZrOH catalyst, which also contains some Zr-stabilized distorted WO$_3$ NPs (see Fig. 13). The supported WZrOH catalyst with the highest TOF corresponds to $\rho_{W,\text{surf}} \sim 6$ W-atoms/nm$^2$, just above monolayer coverage, where crystalline WO$_3$ NPs are expected. The corresponding Raman spectra reveal that generally, only Zr-stabilized WO$_3$ NPs are present for all of the supported WZrOH catalyst samples at $\rho_{W,\text{surf}} \leq 7$ W-atoms/nm$^2$. The lower TOF/TOR activity of the supported WZrOH catalysts with $\rho_{W,\text{surf}} > 9$ W-atoms/nm$^2$ is associated with the presence of bulk-like crystalline WO$_3$ particles, which have only modest acidic activity, and probably are also covering up some of the more active catalytic surface sites (see Fig. 13). The supported WZrOH catalysts are still significantly more active than the model supported WZrO$_2$ catalysts for $\rho_{W,\text{surf}} > 9$ W-atoms/nm$^2$ because of the presence of some distorted Zr-WO$_3$ NPs that are not present in the model supported WZrO$_2$ catalyst system. This also is demonstrated in further studies in which introduction of Zr-WO$_3$ NPs into the model WZrO$_2$ catalyst was found to increase the TOF by as much as a factor of $10^2$.

Previous studies with similar supported WZrOH catalysts have proposed that the acidic catalytic activity of supported WZrOH catalysts for $o$-xylene isomerization and 2-butanol dehydration is only a function $\rho_{W,\text{surf}}$ and corresponds to a two-dimensional surface polytungstate monolayer present in a partially reduced state [18–22,25–29,31]. However, the most active and least active TOFs for supported WZrOH catalysts for methanol dehydration, have the same $\rho_{W,\text{surf}}$ values at $\sim 6$ W-
atoms/nm² (see Fig. 13), indicating that something besides just the \( \rho_{W,\text{surf}} \) parameter influences the catalytic activity. This is further supported by the orders of magnitude difference in TOF/TOR values for the supported WZrOH and model supported WZrO₂ catalysts at the same \( \rho_{W,\text{surf}} \) value (see Fig. 13). The only significant difference between the supported WZrOH series and the model supported WZrO₂ series is the presence of Zr-stabilized distorted WO₃ NPs in the former, which are the catalytically active sites for the supported WZrOH catalysts. The insensitivity of the methanol dehydration TOF to the gas-phase O₂ pressure also is inconsistent with the need for weakly reduced acidic catalytic active sites; \textit{in situ} UV–vis reveals that all of the supported WO₃ species are fully oxidized in the presence of molecular O₂, and reduced sites are present in the absence of O₂. The new model proposed here with Zr-stabilized distorted WO₃ NPs as the catalytic active sites for supported WZrOH catalysts is consistent with all of the experimental observations.

5. Conclusion

The supported WZrOH catalyst system attains monolayer coverage at \( \sim 5 \) W-atoms/nm². In the sub-monolayer region, dehydrated surface WO₃ species and some Zr-stabilized distorted WO₃ NPs are present. The surface WO₃ species rapidly become polymerized with increasing surface coverage, and surface polytungstates become the dominant species at modest surface coverage. Above the monolayer region, the supported WZrOH catalysts have the surface polytungstate monolayers, with distorted Zr-WO₃ NPs and ordered crystalline WO₃ NPs. With increasing \( \rho_{W,\text{surf}} \) and calcination temperature, their relative concentrations vary accordingly: crystalline WO₃ > Zr-stabilized distorted WO₃ NPs > surface polytungstate species. Comparison of the structural characterization information with the acid-catalyzed methanol dehydration performance reveals that the distorted Zr-WO₃ NPs are responsible for the enhanced catalytic activity of supported WZrOH catalysts over the model supported ZrO₂ catalysts. The maximum concentration of the Zr-stabilized distorted WO₃ NPs corresponds to \( \sim 6–7 \) W-atoms/nm², which is just above monolayer coverage.

Acknowledgments

This work was supported by the National Science Foundation’s Nanoscale Interdisciplinary Research Team (NSF-NIRT) under Grant 0609018. The authors thank their colleagues at Lehigh University’s \textit{Operando} Molecular Spectroscopy and Catalysis Laboratory for their helpful discussions, particularly Professor Jih-Mirn Jehng for the amorphous WO₃ Raman studies. Two of the authors (M.S.W. and W.V.K.) acknowledge additional support from SABIC Americas.

References