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# Surface structures of supported tungsten oxide catalysts under dehydrated conditions

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## Abstract

The molecular structures of the  $\text{WO}_3/\text{support}$  ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ ) catalysts under in situ dehydrated conditions have been investigated by Raman spectroscopy. The series of catalysts was synthesized by the aqueous incipient wetness method. The  $\text{WO}_3/\text{support}$  catalysts, with the exception of the  $\text{WO}_3/\text{SiO}_2$  and  $\text{WO}_3/\text{MgO}$  catalysts, possess a highly distorted, octahedrally coordinated surface tungsten oxide species with one short  $\text{W}=\text{O}$  bond (mono-oxo tungsten oxide species) at high surface coverages. The  $\text{WO}_3/\text{SiO}_2$  catalysts exhibit strong Raman features of crystalline  $\text{WO}_3$  particles due to the relative low density and reactivity of the surface hydroxyl groups. The  $\text{WO}_3/\text{MgO}$  catalysts possess non-stoichiometric compounds,  $\text{Mg}_x(\text{WO}_4)_y$  and  $\text{Ca}_x(\text{WO}_4)_y$ , at low tungsten oxide contents and crystalline  $\text{MgWO}_4$  and  $\text{CaWO}_4$  at high tungsten oxide contents. This result is attributed to the high aqueous solubility of  $\text{MgO}$  as well as the  $\text{CaO}$  impurity and the strong acid–base interaction between  $\text{WO}_4^{2-}$  with  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ . The current findings for supported tungsten oxide catalysts parallel the previous findings for supported molybdenum oxide catalysts and reflect the similar surface structural chemistry of these two oxides.

## 1. Introduction

Supported tungsten oxide catalysts are widely used for metathesis and isomerization of alkenes, dehydrogenation of alcohols, and hydrodesulfurization and hydrocracking of heavy fractions in the petroleum industry [1–7]. In addition, the  $\text{WO}_3$  component is added to the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst for the selectively catalytic reduction (SCR) of  $\text{NO}_x$  by  $\text{NH}_3$  due to its high thermal stability and low  $\text{SO}_2$  oxidation activity [8,9].

The industrial importance of supported tungsten oxide catalysts has resulted in a large number of studies concerning their surface properties [10–29] and catalysis [1–9].

The major structural information concerning the surface tungsten oxide species on oxide supports has been derived from Raman spectroscopy because of its ability to discriminate between different tungsten oxide species that may simultaneously be present in the catalysts. The majority of the previous Raman studies on supported tungsten oxide catalysts were performed under ambient conditions where moisture is present on the catalyst surface [9–19]. Relatively few Raman spectroscopic studies have been reported under in situ dehydrated

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conditions, where the adsorbed moisture is removed from catalysts [27–31]. It is generally accepted that the terminal W=O bond of the surface tungsten oxide species shifts to the higher wavenumber region upon dehydration at elevated temperature. The assignment of the Raman band shift upon dehydration is still the subject of debates. Therefore, a systematic investigation is required to better understand the detailed surface structures of the tungsten oxide species on oxide supports.

Most of the previous in situ Raman spectroscopic studies have been devoted to examining the molecular structures of surface tungsten oxide supported on a few oxide supports ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) and limited surface coverage. Therefore, this is the first systematic investigation of the molecular structures of surface tungsten oxide species on different oxide supports at different tungsten oxide contents under in situ dehydrated conditions. The present investigation focuses on the surface structure of the tungsten oxide species on the oxide supports  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ . These oxide supports were chosen because of their widely varying surface characteristics and industrial applications.

## 2. Experimental

### 2.1. Catalyst preparation

A series of the supported tungsten oxide catalysts were prepared by incipient-wetness impregnation method with an aqueous solution of ammonium metatungstate ( $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$ ). The support materials used in this investigation were  $\text{Al}_2\text{O}_3$  (Harshaw,  $180 \text{ m}^2 \text{ g}^{-1}$ ),  $\text{TiO}_2$  (Degussa P-25, anatase/rutile = 66/34,  $55 \text{ m}^2 \text{ g}^{-1}$ ),  $\text{ZrO}_2$  (Degussa,  $39 \text{ m}^2 \text{ g}^{-1}$ ), and  $\text{SiO}_2$  (Cab-O-Sil,  $300 \text{ m}^2 \text{ g}^{-1}$ ). The  $\text{Nb}_2\text{O}_5$  support ( $120 \text{ m}^2 \text{ g}^{-1}$ ) was prepared by the dehydration of hydrated niobium oxide [ $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , Niobium Products Co.] in flowing  $\text{O}_2$  at 393 K for 24 h. The  $\text{MgO}$  support ( $80 \text{ m}^2 \text{ g}^{-1}$ ) was

prepared by the dehydration of magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ , Fluka Chemical Co.] in flowing  $\text{O}_2$  at 973 K for 2 h. After impregnation, the wet samples were initially dried at room temperature for 16 h, further dried at 383 K for 16 h, and then calcined at 773 K for 16 h.

### 2.2. Raman spectroscopy

The Raman spectra of the supported tungsten oxide catalysts were obtained with an  $\text{Ar}^+$  ion laser (Spectra Physics, Model 1877) delivering about 15–40 mW of incident radiation. The excitation line of the laser was 514.5 nm. The scattered radiation from the sample was directed into an optichannel multichannel analyzer with a photodiode array cooled thermoelectrically to 243 K (Princeton Applied Research, OMA III, Model 1463). The in situ Raman spectrometer was equipped with an in situ cell where the temperature and gaseous environment could be controlled. Prior to measurement, the catalysts were dehydrated at 773 K for 1 h in flowing  $\text{O}_2$  and the in situ Raman spectra were collected at room temperature. Ultra-high purity, hydrocarbon free  $\text{O}_2$  (Linde gas) was purged through the cell during the acquisition of the Raman spectra.

## 3. Results

### 3.1. $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts

The in situ Raman spectra of the  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalysts under dehydrated conditions are presented in Fig. 1. The 5%  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalyst possesses Raman bands at 1005,  $\sim 880$ , and  $\sim 300 \text{ cm}^{-1}$  which are assigned to symmetric stretching mode of the terminal W=O, asymmetric mode of the W–O–W, and bending mode of the W=O bonds of the surface tungsten oxide species, respectively. The weak Raman bands at  $\sim 590$  and  $\sim 215 \text{ cm}^{-1}$ , which appear at coverages above 5%, are assigned to the symmetric and bending modes of the W–O–W bonds of the surface tungsten oxide species,

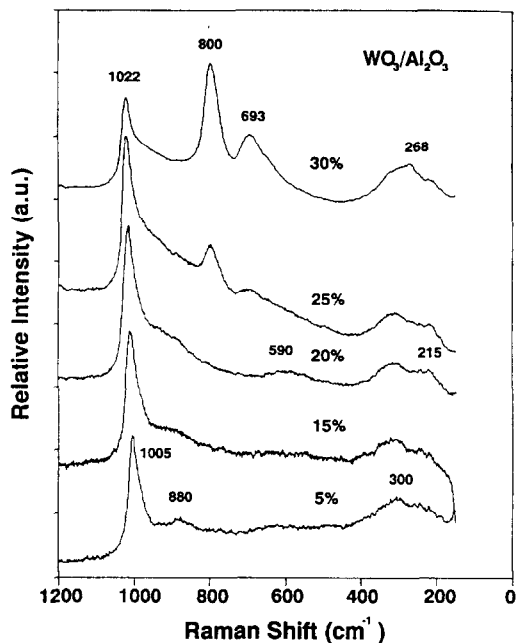


Fig. 1. The in situ Raman spectra of the  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalysts under dehydrated conditions.

respectively. The Raman band due to the terminal  $\text{W}=\text{O}$  bond of the surface tungsten oxide species shifts to the high wavenumber region, from  $1005$  to  $1022\text{ cm}^{-1}$ , with increasing tungsten oxide content. The Raman bands at  $\sim 880$ ,  $\sim 590$ , and  $\sim 215\text{ cm}^{-1}$  increase in intensity with increasing tungsten oxide content. The 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalyst also exhibits very weak Raman bands at  $800$  and  $693\text{ cm}^{-1}$  that are characteristic of microcrystalline  $\text{WO}_3$  particles that did not completely disperse. The 30%  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalyst exhibits stronger Raman features due to crystalline  $\text{WO}_3$  particles at  $800$ ,  $693$ , and  $268\text{ cm}^{-1}$  and reveals that monolayer coverage is exceeded. Monolayer coverage is approximated at 28%  $\text{WO}_3/\text{Al}_2\text{O}_3$ .

### 3.2. $\text{WO}_3/\text{TiO}_2$ catalysts

The in situ Raman spectra of the  $\text{WO}_3/\text{TiO}_2$  catalysts under dehydrated conditions are shown in Fig. 2. The strong support Raman features due to the  $\text{TiO}_2$  limits the collection of the data below  $700\text{ cm}^{-1}$ . The weak Raman band at  $799$

$\text{cm}^{-1}$  is due to the first overtone of the  $395\text{ cm}^{-1}$  band of  $\text{TiO}_2$  (anatase). The  $\text{WO}_3/\text{TiO}_2$  catalysts exhibit a Raman band at  $1010\text{ cm}^{-1}$  for the symmetric stretching mode of the terminal  $\text{W}=\text{O}$  bond of the surface tungsten oxide species independent of the tungsten oxide content. The 10%  $\text{WO}_3/\text{TiO}_2$  catalyst exhibits strong Raman bands due to crystalline  $\text{WO}_3$  at  $800\text{ cm}^{-1}$  as well as the surface tungsten oxide species at  $1010\text{ cm}^{-1}$ .

### 3.3. $\text{WO}_3/\text{Nb}_2\text{O}_5$ catalysts

The in situ Raman spectra of the  $\text{WO}_3/\text{Nb}_2\text{O}_5$  catalysts under dehydrated conditions are shown in Fig. 3. Raman bands due to the  $\text{Nb}_2\text{O}_5$  support have been subtracted from the spectra for the sake of clarity. The weak and broad Raman bands at  $\sim 1018$  and  $\sim 956\text{ cm}^{-1}$  are characteristic of the surface tungsten oxide species. The intensity of the Raman band at  $\sim 956\text{ cm}^{-1}$  increases with increasing tungsten oxide coverage. For the 15%  $\text{WO}_3/\text{Nb}_2\text{O}_5$  catalyst, the weak and sharp Raman band appearing at  $\sim 800\text{ cm}^{-1}$  is characteristic of crystalline  $\text{WO}_3$  particles. This suggests that monolayer coverage of the surface tungsten oxide overlayer

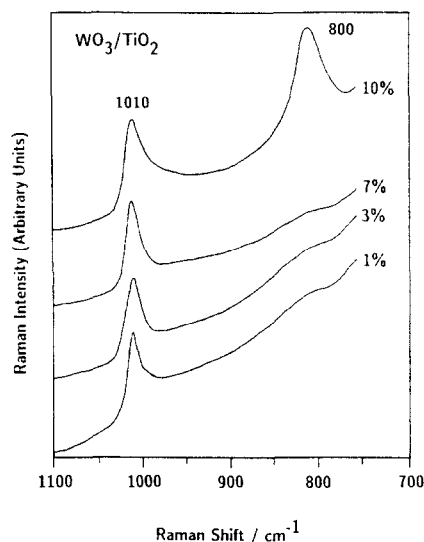


Fig. 2. The in situ Raman spectra of the  $\text{WO}_3/\text{TiO}_2$  catalysts under dehydrated conditions.

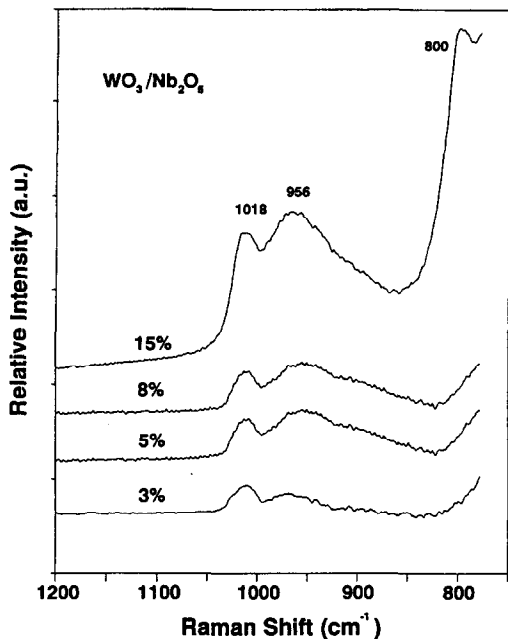


Fig. 3. The in situ Raman spectra of the  $\text{WO}_3/\text{Nb}_2\text{O}_5$  catalysts under dehydrated conditions.

on  $\text{Nb}_2\text{O}_5$  is achieved below 15% tungsten oxide coverage.

### 3.4. $\text{WO}_3/\text{ZrO}_2$ catalysts

The in situ Raman spectra of the  $\text{WO}_3/\text{ZrO}_2$  catalysts under dehydrated conditions are shown in Fig. 4. The strong support Raman bands below  $700\text{ cm}^{-1}$  interfere with the detection of diagnostic Raman bands for the other tungstate functionalities. The weak Raman band due to the  $\text{ZrO}_2$  substrate is observed at  $758\text{--}764\text{ cm}^{-1}$ . The 1%  $\text{WO}_3/\text{ZrO}_2$  catalyst exhibits a Raman band at  $1001\text{ cm}^{-1}$  for the symmetric stretching mode of the terminal  $\text{W}=\text{O}$  bond of the dehydrated surface tungsten oxide species. The 3%  $\text{WO}_3/\text{ZrO}_2$  catalyst possesses Raman bands at  $1009$  and  $804\text{ cm}^{-1}$  which are attributed to the symmetric stretch of the terminal  $\text{W}=\text{O}$  and asymmetric stretch of the  $\text{W}-\text{O}-\text{W}$  bonds, respectively. The symmetric stretching mode of the terminal  $\text{W}=\text{O}$  bond slightly shifts to lower wavenumbers  $1004\text{ cm}^{-1}$ , while the

asymmetric stretching mode of the  $\text{W}-\text{O}-\text{W}$  bond shifts to the higher wavenumber region ( $\sim 875\text{ cm}^{-1}$ ) and becomes broad with increasing the tungsten oxide content to 5%. Higher tungsten oxide loadings result in the formation of crystalline  $\text{WO}_3$  particles which indicates that monolayer surface coverage has been exceeded.

### 3.5. $\text{WO}_3/\text{SiO}_2$ catalysts

The in situ Raman spectra of the  $\text{WO}_3/\text{SiO}_2$  catalysts under dehydrated conditions are presented in Fig. 5. The 1%  $\text{WO}_3/\text{SiO}_2$  catalyst exhibits Raman bands at  $\sim 975$ ,  $\sim 800$ ,  $\sim 715$ ,  $\sim 600$ ,  $\sim 485$ , and  $\sim 450\text{ cm}^{-1}$ . The Raman bands at  $\sim 975$ ,  $\sim 800$ ,  $\sim 600$ ,  $\sim 485$ , and  $\sim 450\text{ cm}^{-1}$  are characteristic of the  $\text{SiO}_2$  support [32]. The Raman bands at  $\sim 975$  and  $\sim 800$  are also due to surface tungsten oxide species and crystalline  $\text{WO}_3$ , respectively, since the bands are sharper than those for only the  $\text{SiO}_2$  support. The Raman band at  $\sim 975\text{ cm}^{-1}$  is assigned to the symmetric stretching mode of the terminal  $\text{W}=\text{O}$  bond of the surface tungsten

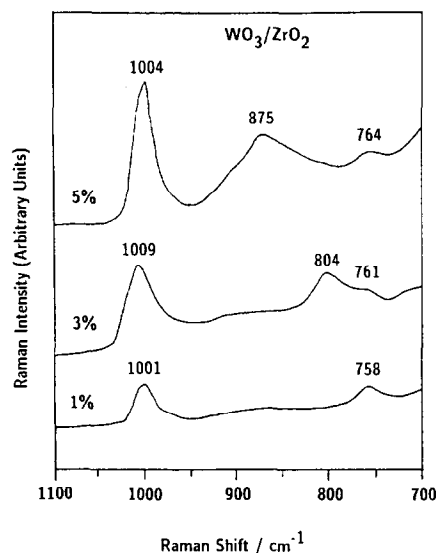


Fig. 4. The in situ Raman spectra of the  $\text{WO}_3/\text{ZrO}_2$  catalysts under dehydrated conditions.

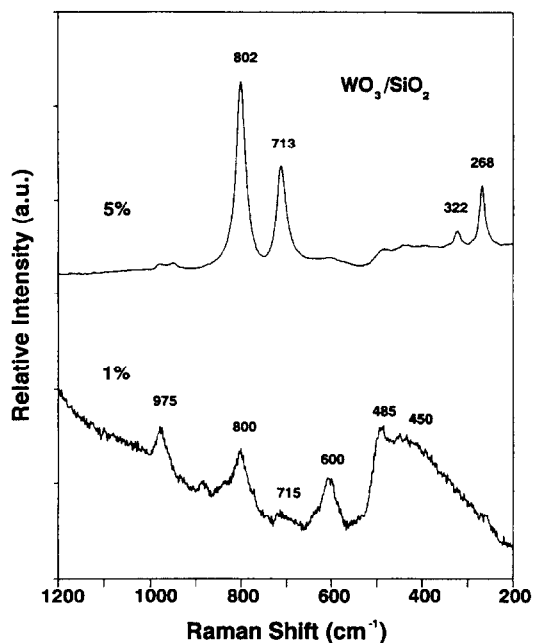


Fig. 5. The in situ Raman spectrum of the  $\text{WO}_3/\text{SiO}_2$  catalysts under dehydrated conditions.

oxide species. The Raman bands at 800 and 715  $\text{cm}^{-1}$  are due to crystalline  $\text{WO}_3$  particles. The intensity of the bands due to the  $\text{SiO}_2$  support decrease with increasing tungsten oxide content because of the stronger signals from the tungsten oxide component. The 5%  $\text{WO}_3/\text{SiO}_2$  catalyst exhibits Raman bands at 802, 713, 322, and 268  $\text{cm}^{-1}$  which are due to crystalline  $\text{WO}_3$  particles.

### 3.6. $\text{WO}_3/\text{MgO}$ catalysts

The in situ Raman spectra of the  $\text{WO}_3/\text{MgO}$  catalysts under dehydrated conditions are shown in Fig. 6. The 1%  $\text{WO}_3/\text{MgO}$  catalyst exhibits a strong Raman band at 895  $\text{cm}^{-1}$  and weak Raman bands at  $\sim 1090$ ,  $\sim 817$ ,  $\sim 390$ ,  $\sim 330$ , and  $\sim 275$   $\text{cm}^{-1}$ . The weak Raman bands at  $\sim 1090$  and  $\sim 275$   $\text{cm}^{-1}$  are characteristic of a crystalline  $\text{CaCO}_3$  impurity present in the  $\text{MgO}$  support [33]. The Raman bands at 895,  $\sim 817$ ,  $\sim 390$ , and  $\sim 330$   $\text{cm}^{-1}$  are assigned to non-stoichiometric compounds of  $\text{Mg}_x(\text{WO}_4)_y$  and

$\text{Ca}_x(\text{WO}_4)_y$ . Catalysts above 3% show Raman bands at  $\sim 915$ ,  $\sim 330$  and  $\sim 217$   $\text{cm}^{-1}$ , which are assigned to crystalline  $\text{CaWO}_4$  [23,34,35]. The Raman band at  $\sim 915$   $\text{cm}^{-1}$  for the  $\text{WO}_3/\text{MgO}$  catalysts above 5% is also characteristic of crystalline  $\text{MgWO}_4$  [23] because the additional Raman band at  $\sim 800$   $\text{cm}^{-1}$  due to crystalline  $\text{MgWO}_4$  is present [23]. Crystalline  $\text{CaWO}_4$  has strong Raman bands at 911 and 338  $\text{cm}^{-1}$  and weak Raman bands at 834, 798, 400, 211, and 118  $\text{cm}^{-1}$ . Crystalline  $\text{MgWO}_4$  exhibits strong Raman bands at 911 and 800  $\text{cm}^{-1}$  and weak Raman bands at 705, 545, 414, 345, and 271  $\text{cm}^{-1}$ . The Raman bands due to the crystalline  $\text{CaWO}_4$  and  $\text{MgWO}_4$  increase at the expense of the bands at 1090,  $\sim 895$ ,  $\sim 817$ , and  $\sim 275$   $\text{cm}^{-1}$  as the tungsten oxide content increases. The Raman band observed at  $\sim 968$   $\text{cm}^{-1}$  for the 5–12%  $\text{WO}_3/\text{MgO}$  catalysts is tentatively assigned to a mildly distorted terminal  $\text{W}=\text{O}$  bond of the surface tungsten oxide species.

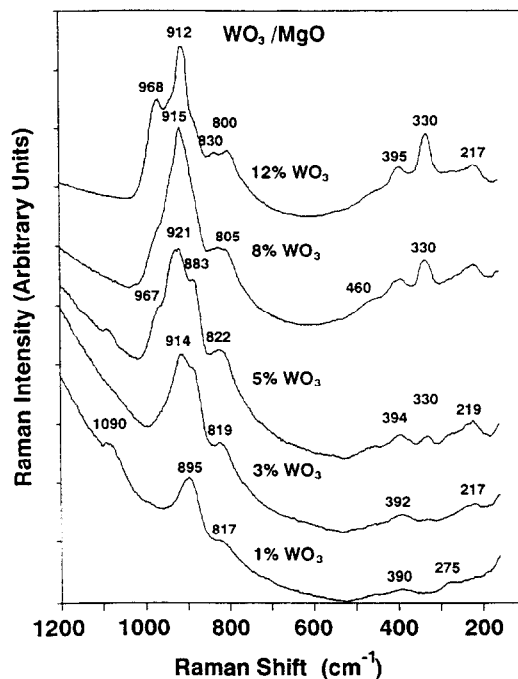


Fig. 6. The in situ Raman spectra of the  $\text{WO}_3/\text{MgO}$  catalysts under dehydrated conditions.

#### 4. Discussion

Many previous studies have proposed that two-dimensional transition metal oxide overlayers are formed when one metal oxide component (i.e.,  $V_2O_5$ ,  $MoO_3$ ,  $CrO_3$ ,  $WO_3$ ,  $Re_2O_7$ ,  $Nb_2O_5$ , etc.) is deposited on a second metal oxide substrate (i.e.,  $Al_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ ,  $SiO_2$ , etc.) [27,29–31,36,37]. However, it was generally accepted that the structures of the surface metal oxide species on oxide supports are not influenced by presence or absence of moisture [27,29–31]. However, recent characterization studies have demonstrated that quite different metal oxide species are formed on oxide supports upon dehydration by performing in situ nuclear magnetic resonance (NMR) [38,39], EXAFS/XANES [40], and Raman spectroscopic studies [28,40–43]. It was concluded from these investigations that under ambient conditions hydrated surface metal oxide species are present on the oxide support surface and are essentially in a solvated state. Consequently, the surface structures of the metal oxide species under ambient conditions are strongly dependent on the net surface pH at PZC (point of zero charge) [44,45]. Upon dehydration at elevated temperature, the hydrated surface metal oxide species are unstable and decompose to form dehydrated surface metal oxide species [28,40–43,46] by direct interaction with the surface OH groups of support (formation of Metal–O–Support bonds) [46]. Kim et al. have shown that for the  $MoO_3/TiO_2$  [47] and  $CrO_3/SiO_2$  [48] catalysts the dehydrated metal oxide species are formed upon dehydration above 573 K by combined Raman spectroscopic and thermal gravimetric studies. The above results suggest that the structural information of metal oxide species should be obtained under dehydrated conditions in order to investigate the relation between the surface structure–reactivity of supported metal oxide catalysts.

The present in situ Raman spectroscopy studies revealed that the  $WO_3$ /support ( $Al_2O_3$ ,  $TiO_2$ ,  $Nb_2O_5$ , and  $ZrO_2$ ) catalysts possess a

major Raman band at  $\sim 1000$ – $1020\text{ cm}^{-1}$  due to the terminal  $W=O$  bond of the dehydrated tungsten oxide species. In addition, previous IR studies showed that the  $WO_3/Al_2O_3$  and  $WO_3/TiO_2$  catalysts exhibit an IR band due to the terminal  $W=O$  bond of the dehydrated surface tungsten oxide species at 1010–1022 [28,29,49] and  $1015\text{ cm}^{-1}$  [49], respectively. The Raman and IR bands due to the terminal  $W=O$  bond, at corresponding tungsten oxide content, are observed at similar frequencies. The correspondence of the terminal  $W=O$  frequency in the Raman and IR spectra suggests that mono-oxo tungsten oxide species are present on the oxide support. If a di-oxo ( $O=W=O$ ) tungsten oxide species were present, it should give rise to two Raman and IR bands due to the symmetric and asymmetric stretching modes of the  $O=W=O$  bond with different relative intensities and wavenumbers ( $30$ – $50\text{ cm}^{-1}$  difference) [49–51]. Moreover, Horsley et al. [15] found with in situ XANES that the surface tungsten oxide species in  $WO_3/Al_2O_3$  catalysts, calcined at 773 K, is predominantly present as a highly distorted, octahedrally coordinated tungsten oxide species at high tungsten oxide coverages and a distorted tetrahedral species at tungsten oxide coverages below 1/3 monolayer. Hilbrig et al. [52] found with in situ XANES that the surface tungsten oxide species of  $WO_3/TiO_2$  catalysts, calcined at 673 K, is present as a distorted, pentahedral coordinated tungsten oxide species at high tungsten oxide coverages and a distorted tetrahedral species at tungsten oxide coverages below 1/3 monolayer. Hilbrig et al. [52] also predicted the same situation for tungsten oxide on  $Al_2O_3$ . These in situ XANES and Raman results suggest that the structure of the surface tungsten oxide species on  $Al_2O_3$  and  $TiO_2$  as well as  $Nb_2O_5$  and  $ZrO_2$  are a function of surface tungsten oxide coverage.

In addition to the major Raman band at  $\sim 1000$ – $1020\text{ cm}^{-1}$ , the tungsten oxide supported  $Nb_2O_5$ ,  $ZrO_2$ ,  $Al_2O_3$ , and  $TiO_2$  catalysts also exhibit a weaker Raman band at  $\sim 800$ – $960$

$\text{cm}^{-1}$ . This band increases in intensity with increasing tungsten oxide coverage in the order  $\text{Nb}_2\text{O}_5 > \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{TiO}_2$  which indicates the presence of a second tungsten oxide species. The Raman band at  $\sim 800\text{--}960 \text{ cm}^{-1}$  is assigned to the asymmetric mode of a W–O–W linkage, suggesting the second tungsten oxide species consists of a surface polytungsten oxide species on the oxide support [28]. The Raman band at  $\sim 956 \text{ cm}^{-1}$  of the  $\text{WO}_3/\text{Nb}_2\text{O}_5$  catalysts is more intense than the Raman band at  $\sim 1018 \text{ cm}^{-1}$  for tungsten oxide coverages above 3%. The Raman band at  $804 \text{ cm}^{-1}$  for the 3%  $\text{WO}_3/\text{ZrO}_2$  catalyst becomes broadened and shifts to the higher wavenumber ( $875 \text{ cm}^{-1}$ ) region when the tungsten oxide coverage increases to 5%. For tungsten oxide contents above 5%  $\text{WO}_3/\text{Al}_2\text{O}_3$ , additional weak Raman bands are present at  $\sim 590$  and  $215 \text{ cm}^{-1}$ . These bands increase as the band at  $\sim 880 \text{ cm}^{-1}$  increases with tungsten oxide coverage and are assigned to the symmetric and bending modes of the W–O–W linkage, respectively. The  $\text{WO}_3/\text{TiO}_2$  catalysts exhibit a very weak Raman band at  $\sim 880 \text{ cm}^{-1}$  which suggests the surface tungsten oxide species is present as a less polymerized surface tungsten oxide species.

Silica supported metal oxides ( $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$ , and  $\text{WO}_3$ ) generally possess very poorly dispersed metal oxide phases that are present as corresponding crystalline metal oxide particles when prepared by impregnation or the incipient wetness method [42,43,48,53,54]. Recently, Ekerdt et al. [46,53] demonstrated that the preparation method and precursor are important parameters that control the dispersion of surface molybdenum and tungsten oxide species on  $\text{SiO}_2$ . They have successfully prepared highly dispersed  $\text{MoO}_3/\text{SiO}_2$  and  $\text{WO}_3/\text{SiO}_2$  catalysts up to 7.8 [46] and 9.6 wt% [55], respectively, without formation of crystalline  $\text{MoO}_3$  and  $\text{WO}_3$  by using a non-aqueous preparation method involving organometallic precursors. They [55] also reported that the surface tungsten oxide species on silica possesses an isolated, octahedrally coordinated tungsten oxide struc-

ture with one short W=O bond ( $\nu_s(\text{W}=\text{O})$ :  $982\text{--}984 \text{ cm}^{-1}$ ) regardless of the tungsten oxide content. The current studies confirm that aqueous preparation of  $\text{WO}_3/\text{SiO}_2$  catalysts with ammonium metatungstate favors the formation of crystalline  $\text{WO}_3$  particles. The 1%  $\text{WO}_3/\text{SiO}_2$  catalysts contains both surface tungsten oxide species, Raman band at  $\sim 975 \text{ cm}^{-1}$ , and crystalline  $\text{WO}_3$  particles, Raman bands at  $\sim 800$  and  $\sim 715 \text{ cm}^{-1}$ . The 5%  $\text{WO}_3/\text{SiO}_2$  catalyst is dominated by the strong Raman signals of the crystalline  $\text{WO}_3$  particles and the surface tungsten oxide species are not detectable. Thus, the preparation method is responsible for controlling the dispersion of metal oxides on  $\text{SiO}_2$ .

The  $\text{WO}_3/\text{MgO}$  catalysts showed very different Raman features compared to the other supported tungsten oxide catalysts. The absence of the  $980\text{--}1020 \text{ cm}^{-1}$  Raman band due to the symmetric stretching mode of the terminal W=O bond for the dehydrated surface tungsten oxide species indicates that different tungsten oxide species are present on the MgO support. The Raman band at  $968 \text{ cm}^{-1}$  for the 5–12%  $\text{WO}_3/\text{MgO}$  catalysts is due to a mildly distorted W=O bond of the dehydrated surface tungsten oxide species since this band shifts upon hydration. Wang [29] and Kim et al. [42,55] have demonstrated that MgO and the CaO impurity are readily soluble in water and easily make a compound with  $\text{MoO}_4^{2-}(\text{aq})$ ,  $\text{CrO}_4^{2-}(\text{aq})$ ,  $\text{ReO}_4^-(\text{aq})$ ,  $\text{WO}_4^{2-}(\text{aq})$ , and  $\text{VO}_4^{3-}(\text{aq})$  during aqueous preparations. The formation of such compounds is strongly dependent on the pH of the impregnating solution, calcination temperature and time [42,55]. The Raman band positions for 1%  $\text{WO}_3/\text{MgO}$  catalyst does not correspond with the Raman bands of crystalline  $\text{CaWO}_4$  and  $\text{MgWO}_4$ . The different Raman features for the 1%  $\text{WO}_3/\text{MgO}$  catalysts are attributed to the formation of a solid solution of tungsten oxide with the MgO support due to the strong acid–base interaction of  $\text{WO}_4^{2-}(\text{aq})$  with MgO as well as nonstoichiometric compounds such as  $\text{Mg}_x(\text{WO}_4)_y$ . At high tungsten oxide

contents, both  $\text{CaWO}_4$  and  $\text{MgWO}_4$  compounds are present. A similar trend is observed for the magnesia supported  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{Re}_2\text{O}_7$ , and  $\text{CrO}_3$  catalysts [55,56].

Supported tungsten oxide and molybdenum oxide catalysts behave similarly on the oxide supports  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ . The structures of the dehydrated surface tungsten and molybdenum oxide species on the oxide supports are both dependent on tungsten and molybdenum oxide [56–58] coverage, respectively. At low surface tungsten and molybdenum oxide coverages, a highly distorted, tetrahedral and isolated structure is dominant on the oxide supports  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{ZrO}_2$ . As the tungsten and molybdenum oxide contents approach monolayer coverage, polytungsten and polymolybdenum oxide species also appear on the supports with a highly distorted, octahedral mono-oxo structure. Both isolated surface tungsten and molybdenum oxide species and crystallites are present on  $\text{SiO}_2$ , and their relative populations depend on the specific preparation method. Magnesium oxide supported tungsten and molybdenum oxide catalysts possess both surface oxide species and compound with  $\text{MgO}$  and the  $\text{CaO}$  impurity. The analogous behavior of the supported tungsten oxide and molybdenum oxide catalysts reflects the similar solid state chemistry of the two oxides [57]. Also, the monolayer densities of the supported tungsten and molybdenum oxide catalysts [57] are very similar as shown in Tables 1 and 2, respectively. Since tungsten and molybdenum oxide supported  $\text{MgO}$  and  $\text{SiO}_2$  catalysts form compounds and crystals at mono-

Table 1  
The surface density of supported  $\text{WO}_3$  catalysts at monolayer coverage

Support	Surface area ( $\text{m}^2/\text{g}$ )	Monolayer loading (wt% $\text{WO}_3$ )	Surface density ( $\text{W}/\text{nm}^2$ )
$\text{Al}_2\text{O}_3$	180	~ 28	4.0
$\text{TiO}_2$	55	~ 9	4.2
$\text{ZrO}_2$	39	~ 6	4.0
$\text{Nb}_2\text{O}_5$	120	~ 14	3.0

Table 2

The surface density of supported  $\text{MoO}_3$  catalysts at monolayer coverage

Support	Surface area ( $\text{m}^2/\text{g}$ )	Monolayer loading (wt% $\text{MoO}_3$ )	Surface density ( $\text{Mo}/\text{nm}^2$ )
$\text{Al}_2\text{O}_3$	180	~ 20	4.6
$\text{TiO}_2$	55	~ 6	4.6
$\text{ZrO}_2$	39	~ 4	4.3
$\text{Nb}_2\text{O}_5$	55	~ 6	4.6

layer coverage, respectively, their monolayer densities are not listed in Tables 1 and 2.

## 5. Conclusion

A series of supported tungsten oxide catalysts on different oxide supports ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ ) was structurally characterized by in situ Raman spectroscopy. The surface tungsten oxide species on  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{ZrO}_2$  possess a highly distorted, octahedrally coordinated surface tungsten oxide structure with one short  $\text{W}=\text{O}$  bond (mono-oxo species) at high surface coverages. The extent of the polymerization of the surface tungsten oxide species is strongly dependent on the tungsten oxide coverage and the specific oxide support. At low surface coverages, an isolated, tetrahedral, coordinated surface tungsten oxide species appears to predominate. The  $\text{WO}_3/\text{SiO}_2$  catalyst contains crystalline  $\text{WO}_3$  because of the lower density and reactivity of the silica surface  $\text{OH}$  groups during the aqueous preparation method. The  $\text{WO}_3/\text{MgO}$  catalysts possess  $\text{MgWO}_4$  and  $\text{CaWO}_4$  compounds due to the high solubility of  $\text{MgO}$  and impurity  $\text{CaO}$  in aqueous solutions and the strong acid–base interaction between tungsten oxide and  $\text{MgO}/\text{CaO}$ . The presence of some surface tungsten oxide species on  $\text{MgO}$  was also detected. The current findings for supported tungsten oxide catalysts essentially follow the behavior previously found for the corresponding supported molybdenum oxide catalysts.



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