# Preparation and characterization of $WO_3$ / $SiO_2$ catalysts

Du Soung Kim, Marlene Ostromecki, Israel E. Wachs [1]

*Zettlemoyer Center for Surface Studies, Department of Chemical Engineering,*
*Lehigh University, Bethlehem, PA 18015, USA*

Steve D. Kohler and John G. Ekerdt

*Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78721, USA*

Received 23 February 1995; accepted 19 April 1995

Two sets of $WO_3/SiO_2$ catalysts were prepared from $(NH_4)_6H_2W_{12}O_{40}$ (aqueous method) and $W(\eta^3\text{-}C_3H_5)_4$ (non-aqueous method). The molecular structures and dispersions of the surface tungsten oxide species for the $WO_3/SiO_2$ catalysts under ambient and in situ dehydrated conditions were investigated by Raman spectroscopy. The samples prepared from $(NH_4)_6H_2W_{12}O_{40}$ (aqueous method) exhibit very strong Raman features due to the presence of crystalline $WO_3$ and the samples prepared from $W(\eta^3\text{-}C_3H_5)_4$ (non-aqueous method) do not possess crystalline $WO_3$. These results suggest that the preparation method exerts an influence on the dispersion of the surface tungsten oxide species on $SiO_2$. The surface tungsten oxide species under ambient conditions possess polytungstate clusters, $W_{12}O_{42}^{12-}$, on the silica support. Upon dehydration at elevated temperatures, the hydrated polytungstate clusters decompose and interact with the silica support via the formation of isolated, octahedrally coordinated tungsten oxide species.

**Keywords:** tungsten oxide; silica; Raman spectroscopy; surface structure; dispersion

## 1. Introduction

Silica supported metal oxide catalysts ($WO_3$, $V_2O_5$, $CrO_3$, $MoO_3$, $Re_2O_7$) have usually been prepared by aqueous impregnation or incipient wetness methods. Unfortunately, these preparation methods give poorly dispersed surface metal oxide species due to the weak interaction between the surface metal oxides and silica [1]. Consequently, there has been much interest in less conventional preparation methods involving non-aqueous organometallic precursors to improve the dispersion of the surface oxide species on silica by suppressing the formation of crystalline metal oxides [2–7]. Recently, Roark et al. [2] have successfully prepared highly dispersed $Mo^{6+}/SiO_2$ catalysts by a non-aqueous preparation method using

---

[1] To whom correspondence should be addressed.
Research and Development Division, Daelim Engineering, Co., Ltd. #17-5, Yoido-dong, Yongdungpo-ku, Seoul, 150-010, Korea.

$Mo_2(\eta^3\text{-}C_3H_5)_4$ or $(\eta^5\text{-}C_2H_5)_2Mo_2(CO)_4$ without formation of crystalline $MoO_3$ up to 7.8 wt% Mo, which corresponds to the silanol density of silica. The study suggests that the dispersion of the surface metal oxide species on $SiO_2$ is strongly dependent on the preparation method.

In the past few years, Raman spectroscopy has played an important role in the characterization of supported metal oxide catalysts. The advantage of Raman spectroscopy is that it is able to discriminate among the various metal oxide phases simultaneously present in such multicomponent systems as well as provide molecular level structural information. Another advantage of the Raman characterization technique is that the experiments can also be performed in situ with no stringent requirements on the sample preparation or the sample environment within the cell.

The present investigation reports on the influence of the preparation method on the dispersion of the tungsten oxide species and the molecular structures of the surface tungsten oxide species on $SiO_2$ under ambient and in situ, dehydrated, conditions.

## 2. Experimental

Davison 952 silica gel was washed in dilute sulfuric acid to remove impurities [8,9]. The BET area was 317 $m^2/g$ before acid-washing and 329 $m^2/g$ after washing. The tungsten was loaded onto the silica using two different techniques. The first involved wet impregnation of the silica with an aqueous solution of ammonium metatungstate, $(NH_4)_6H_2W_{12}O_{40}$, and the second involved attachment of tungsten using $W(\eta^3\text{-}C_3H_5)_4$.

Ammonium metatungstate was dissolved in just enough water to wet the silica. The silica pores were filled with aqueous solution, dried at 140°C for 4 h, and calcined at 500°C for 6 h in hydrocarbon-free air. The procedure with $W(\eta^3\text{-}C_3H_5)_4$ was similar to the one developed for $Mo_2(\eta^3\text{-}C_3H_5)_4$ [7]. $W(\eta^3\text{-}C_3H_5)_4$ was synthesized by reaction of $WCl_4$, dissolved in diethyl ether, with $C_3H_5MgBr$ at −23°C for 1 h. Pentane solutions of $W(\eta^3\text{-}C_3H_5)_4$ were added to silica at 0°C. The exchange reaction of $C_3H_5$ ligands with silica OH groups was complete within 20 min. Excess pentane was filtered, and samples were evacuated for 1 h. Samples were then ramped at 5°C/min in pure $H_2$ to 550°C and held at this temperature for 1 h. The W content was determined by Galbraith Labs.

The Raman spectra of the $WO_3/SiO_2$ catalysts under ambient and in situ dehydrated conditions were obtained with an $Ar^+$ ion laser (Spectra Physics model 171) delivering about 15–40 mW of incident radiation. The excitation line of the Raman scattering was 514.5 nm. The scattered radiation from the sample was directed into a Spex Triplemate spectrometer (model 1877) equipped with an intensified photodiode array detector cooled thermoelectrically to 238 K. Prior to the in situ measurements, the samples were dehydrated at 773 K for 1 h in flowing $O_2$, and the

Raman spectra of the dehydrated samples were subsequently collected at room temperature. Ultrahigh-purity, hydrocarbon-free oxygen was purged through the cell during the acquisition of the Raman spectra [10].

## 3. Results

The Raman spectra of the $WO_3/SiO_2$ catalysts prepared from the non-aqueous method, using $W(\eta^3\text{-}C_3H_5)_4$, under ambient conditions are shown in fig. 1. The Raman spectra of the $WO_3/SiO_2$ catalysts possess Raman bands that originate from the $SiO_2$ support as well as the surface tungsten oxide species. The broad Raman bands at ~800, ~609, ~486, and ~389 $cm^{-1}$ are characteristic Raman features of the silica support [11] and the intensity of these bands decreases upon increasing the tungsten oxide content. The Raman bands due to the symmetric stretching mode of the terminal W=O bond and deformation mode of the W–O–W bond of the hydrated surface tungsten oxide species are observed at 967–973 and 215 $cm^{-1}$, respectively. No Raman bands due to crystalline $WO_3$ compounds (~800, 705, 265 $cm^{-1}$) are observed. The in situ Raman spectra of the $WO_3/SiO_2$

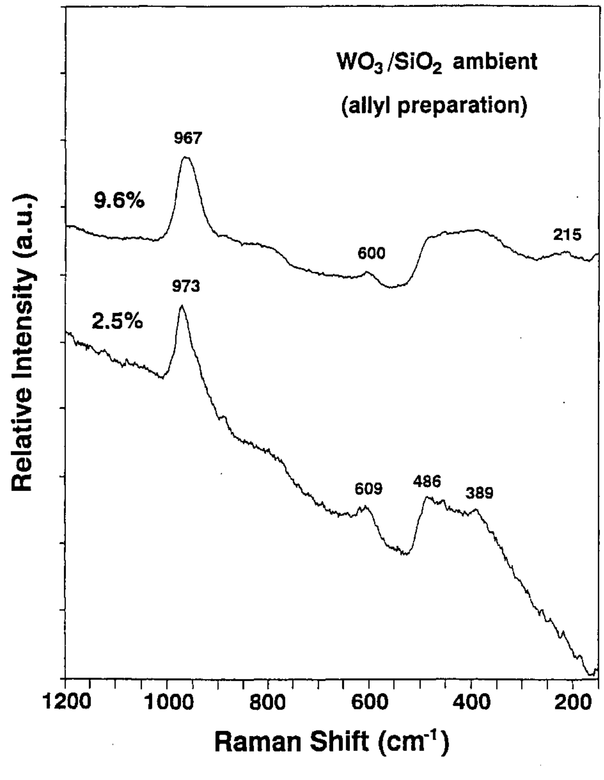

Fig. 1. Raman spectra of $WO_3/SiO_2$ catalysts prepared by the non-aqueous method using $W(\eta^3\text{-}C_3H_5)_4$ under ambient conditions.

catalysts prepared from the non-aqueous method, using $W(\eta^3\text{-}C_3H_5)_4$ are shown in fig. 2. Upon dehydration at elevated temperature, the major Raman band due to the hydrated surface tungsten oxide species becomes sharper and shifts from 967–973 to 982–984 $cm^{-1}$. The minor Raman band at 215 $cm^{-1}$ associated with W–O–W bonds is absent for the dehydrated surface tungsten oxide species on $SiO_2$. In addition, no Raman bands due to crystalline $WO_3$ are observed under the in situ dehydrated conditions.

The Raman spectra of the $WO_3/SiO_2$ catalysts prepared from the aqueous method, using $(NH_4)_6H_2W_{12}O_{40}$, under ambient and in situ dehydrated conditions are shown in fig. 3. The Raman spectra of the $WO_3/SiO_2$ catalysts under ambient conditions possess weak Raman bands due to the surface tungsten oxide species on $SiO_2$ at 961 ($\nu_s$ (W=O)) and 321 $cm^{-1}$. However, the Raman spectra of the $WO_3/SiO_2$ catalysts also exhibit very strong Raman bands due to crystalline $WO_3$ at 802–804, 706–709, and 267–271 $cm^{-1}$, which are assigned to the symmetric stretching mode of the W–O, bending mode of the W–O, and deformation mode of the W–O–W bonds, respectively [12]. Additional minor Raman bands for $WO_3$ are observed at ~610 and 321–325 $cm^{-1}$. The Raman spectrum of the 3.8% $WO_3/SiO_2$ catalysts under in situ dehydrated conditions, where water molecules are desorbed from the

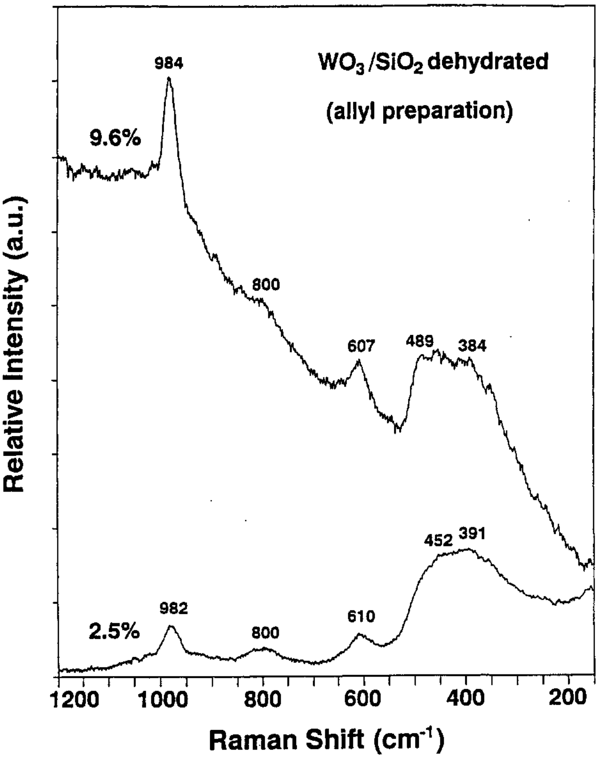

Fig. 2. Raman spectra of $WO_3/SiO_2$ catalysts prepared by the non-aqueous method using $W(\eta^3\text{-}C_3H_5)_4$ under in situ dehydrated conditions.

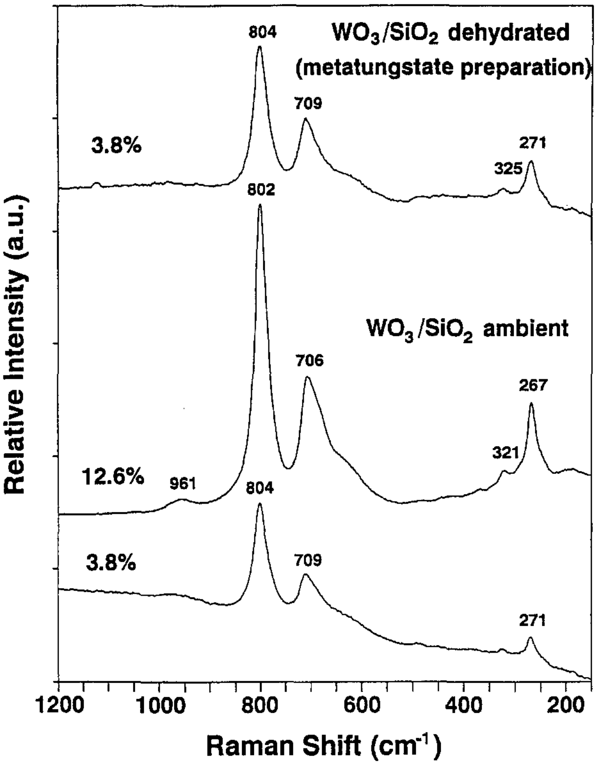

Fig. 3. Raman spectra of $WO_3/SiO_2$ catalysts prepared by the aqueous method using $(NH_4)_6H_2W_{12}O_{40}$ under ambient and in situ dehydrated conditions.

surface, possesses very strong Raman bands due to crystalline $WO_3$. The Raman band due to the dehydrated surface tungsten oxide species ($\nu_s$(W=O): 984 $cm^{-1}$) (see fig. 2) on $SiO_2$ may be present, but it would be obscured by the very strong Raman bands of crystalline $WO_3$. The observation of very strong Raman features due to crystalline $WO_3$ for the $WO_3/SiO_2$ catalysts prepared from the aqueous preparation method indicates the formation of a very poorly dispersed supported tungsten oxide phase on $SiO_2$.

## 4. Discussion

The tungsten oxide species present in an aqueous solution varies as functions of the pH of the impregnating solution and concentration [13,14]. The equilibrium between monomeric $WO_4^{2-}$ and polymeric $W_{12}O_{42}^{12-}$ species above 0.1 M is as follows:

$$12WO_4^{2-} + 12H^+ \rightleftharpoons W_{12}O_{42}^{12-} + 6H_2O \qquad (1)$$

The tetrahedrally coordinated $WO_4^{2-}$ is the predominant species in basic solution and possesses Raman bands at 931 ($\nu_s$(W=O)), 834 ($\nu_{as}$(W=O)), and 326 $cm^{-1}$ ($\delta$(W=O)) [12]. On the other hand, the octahedrally coordinated polytungstate, $W_{12}O_{42}^{12-}$, is the predominant species in acidic solution and possesses Raman bands at 980–960 $cm^{-1}$ ($\nu$(W=O)), 330–190 $cm^{-1}$ (W–O–W mode) [11].

The surface tungsten oxide species under ambient conditions possesses Raman bands due to the polytungsten oxide species, $W_{12}O_{42}^{12-}$, at 961–973 and 215 $cm^{-1}$ (see fig. 1). No Raman evidence for the existence of the tetrahedrally coordinated tungsten oxide species, $WO_4^{2-}$, was found in the spectra. Recently, Wachs et al. [10,15–17] have demonstrated that under ambient conditions the surface of the support is hydrated and the surface metal oxide ($V_2O_5$, $CrO_3$, $MoO_3$, $WO_3$, and $Re_2O_7$) overlayers are essentially in an aqueous medium. Consequently, the structure of the metal oxide overlayer follows the metal oxide aqueous chemistry as a function of the net surface pH at point of zero charge (PZC). The $SiO_2$ support used in this investigation possesses an acidic pH at PZC (pH = 3.7) and the addition of the tungsten oxide (PZC of $W^{6+}$; pH = 0.4–1.0 [18]) results in further decrease of the surface net pH at PZC for the $WO_3/SiO_2$ catalyst [17]. Therefore, the presence of only hydrated polytungsten oxide species for $WO_3/SiO_2$ catalysts under ambient conditions is attributed to the low net surface pH at PZC of these catalysts. In addition, the molecular structures of the surface tungsten oxide species under ambient conditions on $SiO_2$ are found to be independent of the preparation method.

The Raman spectra of the $WO_3/SiO_2$ under in situ dehydrated conditions possess only a single Raman band due to the dehydrated surface tungsten oxide species on the silica support at 982–984 $cm^{-1}$ (see fig. 2). This observation suggests that the dehydrated surface tungsten oxide species possesses mono-oxo tungsten oxide species (W=O) on $SiO_2$ since di-oxo tungsten oxide species (O=W=O) should give rise to two Raman bands due to the symmetric and asymmetric stretching modes. Hardcastle et al. [19] have proposed that the mono-oxo tungsten oxide species possesses a highly distorted octahedral structure with one short W=O bond and one long opposite W–O bond on the base of the diatomic approximation method. In addition, the absence of characteristic Raman features due to the bending mode of W–O–W linkage at 215 $cm^{-1}$ over $WO_3/SiO_2$ indicates that the surface tungsten oxide species appears to be isolated on $SiO_2$. Thus, the dehydrated surface tungsten oxide species possesses an isolated, octahedrally coordinated structure.

The Raman spectra of the $WO_3/SiO_2$ catalysts showed that the preparation method exerts a strong influence on the dispersion of the surface tungsten oxide species on $SiO_2$. The $WO_3/SiO_2$ catalysts prepared from the aqueous method using $(NH_4)_6H_2W_{12}O_{40}$ possess very strong Raman features due to crystalline $WO_3$ and no Raman bands due to crystalline $WO_3$ are observed for the $WO_3/SiO_2$ catalysts prepared from the non-aqueous method using $W(\eta^3\text{-}C_3H_5)_4$. This result suggests that the catalysts prepared from a non-aqueous method possess much higher dispersion of the surface tungsten oxide species than those prepared from the aqueous method. The achievement of highly dispersed surface tungsten oxide species for the $WO_3/SiO_2$ catalysts prepared from the non-aqueous method is attributed to the inherent chemical reactivity of the $W(\eta^3\text{-}C_3H_5)_4$ solution with $SiO_2$ [7].

## Acknowledgement

This work was supported by the US Department of Energy under grants DEFG02-93ER14350 and DEFG05-86ER13604.

## References

[1] S.R. Stampfl, Y. Chen, J.A. Dumesic, C. Niu and C.G. Hill Jr., J. Catal. 105 (1987) 445.
[2] R.D. Roark, S.D. Kohler, J.G. Ekerdt, D.S. Kim and I.E. Wachs, Catal. Lett. 16 (1992) 77.
[3] Y. Iwasawa, in: *Advances in Catalysis*, Vol. 35 (Academic Press, New York, 1987) p. 265.
[4] Y.I. Yermakov, Catal. Rev. Sci. Eng. 13 (1976) 77.
[5] J.P. Candlin and H. Thomas, Adv. Chem. Ser. 132 (1974) 212.
[6] L. Rodrigo, K. Marcinkowska, A. Adnot, P.C. Roberge, S. Kaliaguine, J.M. Stencil, L.E. Makovsky and J.R. Diehl, J. Phys. Chem. 90 (1986) 2690.
[7] C.C. Williams, J.G. Ekerdt, J.M. Jehng, F.D. Hardcastle, A.M. Turek and I.E. Wachs, J. Phys. Chem. 95 (1991) 8781.
[8] C.C. Williams and J.G. Eckerdt, J. Catal. 141 (1993) 430.
[9] N. Spencer, J. Catal. 109 (1988) 187.
[10] D.S. Kim and I.E. Wachs, J. Catal. 141 (1993) 419.
[11] F.D. Hardcastle and I.E. Wachs, J. Mol. Catal. 46 (1988) 173.
[12] S.S. Chan, I.E. Wachs and L.L. Murrell, J. Catal. 90 (1984) 150.
[13] W.P. Griffith and P.J.B.J. Lesniak, J. Chem. Soc. A (1969) 1066.
[14] C.F. Baes and R.E. Mesmer, in: *Hydrolysis of Cations* (Wiley, New York, 1986).
[15] G. Deo and I.E. Wachs, J. Phys. Chem. 95 (1991) 5889.
[16] D.S. Kim and I.E. Wachs, J. Catal. 136 (1992) 539.
[17] S.D. Kohler, J.G. Ekerdt, D.S. Kim and I.E. Wachs, Catal. Lett. 16 (1992) 231.
[18] G.A. Parks, Chem. Rev. 65 (1965) 177.
[19] F.D. Hardcastle, PhD Thesis, Lehigh University, USA (1990);
F.D. Hardcastle and I.E. Wachs, J. Raman Spectry., in press.