

## Relative Raman Cross-Sections of Tungsten Oxides: [WO<sub>3</sub>, Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> and WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>]

Laser Raman spectroscopic studies of alumina-supported WO<sub>3</sub> catalysts have shown that three different tungsten oxide phases are present in WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts: WO<sub>3</sub>, Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>, and a surface tungsten oxide species (1-8). The concentrations of these phases in WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts depend on tungsten oxide loading and temperature of calcination. Previous studies have shown that Raman spectroscopy is more sensitive to WO<sub>3</sub> and Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> than the surface tungsten oxide complex. No attempt, however, has been made to estimate the relative Raman cross sections of these tungsten oxide phases. This information is essential for a model to be developed of the WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system. In this note the relative Raman intensities of WO<sub>3</sub>, Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>, and the surface tungsten oxide species on alumina are determined, and this information is used to examine previous conclusions about the WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system.

Samples of pure WO<sub>3</sub> and pure Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> were obtained from Cerac and their structures were confirmed by X-ray diffraction. A 10 wt% WO<sub>3</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Harshaw, Al-4104E, 220 m<sup>2</sup>/g) was prepared by the incipient wetness or dry impregnation method using ammonium metatungstate (Sylvania, Inc.) and subsequently calcining at 500, 1000, and 1050°C for 16 h. In addition, 15 and 25 wt% WO<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Engelhard Industries, reforming grade) samples were prepared on the 180 m<sup>2</sup>/g alumina support. The surface area of the 15 and 25% supported oxides were reduced to 120 m<sup>2</sup>/g by steaming these WO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> samples at 760°C as described elsewhere (7). An argon ion laser (Spectra Physics, Model 165) was tuned to the 514.5-nm line for excitation. A prism monochromator

(Anaspec Model 300S) which has a typical band width of 0.3 nm was used to remove the laser plasma lines. A cylindrical lens (*f* = 250 mm) and a variable spherical lens (*f* = 90-100 mm) were used to achieve an elliptically focused image on the sample. Each sample of about 0.2 g was pelletized under 10 kpsi pressure into a 13-mm-diameter wafer for mounting on a sample holder capable of spinning. The laser power at the sample location was changed by inserting neutral density filters. The scattered light was collected by a lens (*F*/1.2, *f*/55 mm) held at about 45° with respect to the excitation. The Raman spectrometer was a triple monochromator (Instruments SA, Model DL203) equipped with holographic gratings and F4 optics. The spectrometer was coupled to an optical multichannel analyzer (Princeton Applied Research, Model OMA2) equipped with an intensified photodiode array detector cooled to -15°C. The total accumulation time needed for each spectrum reported here typically was about 100 sec or less. The digital display of the spectrum was calibrated to give 1.7 cm<sup>-1</sup>/channel whereas the overall spectral resolution was about 6 cm<sup>-1</sup>.

The Raman spectra of WO<sub>3</sub>, Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>, and 10% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> are presented in Fig. 1. The WO<sub>3</sub> structure (distorted ReO<sub>3</sub> structure) is made up of distorted corner-shared WO<sub>3</sub> octahedra. The major vibrational modes of WO<sub>3</sub> are located at 808, 714, and 276 cm<sup>-1</sup>, and have been assigned to the W=O stretching mode, the W=O bending mode, and the W—O—W deformation mode, respectively (9). Other minor bands are at 608, 327, 243, 218, 185, and 136 cm<sup>-1</sup>. The Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> is a defect scheelite structure (distorted CaWO<sub>4</sub> structure) composed

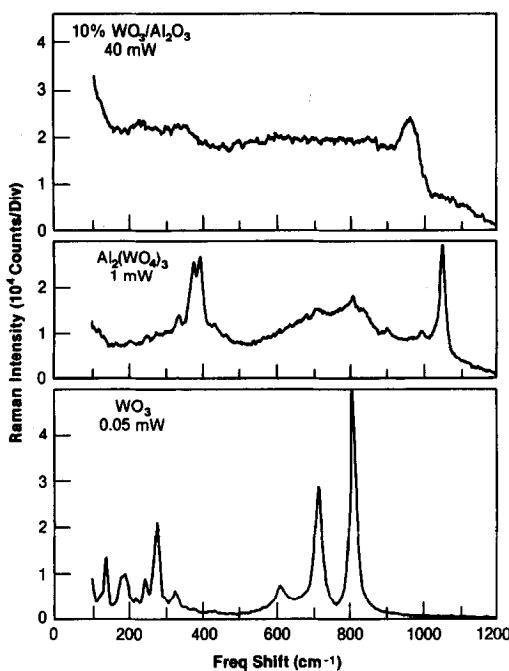


FIG. 1. Raman spectra of tungsten oxides [ $\text{WO}_3$ ,  $\text{Al}_2(\text{WO}_4)_3$ , and 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  ( $500^\circ\text{C}$ )].

of distorted, isolated tetrahedral tungstate. The major Raman peaks of  $\text{Al}_2(\text{WO}_4)_3$  are assignable by comparison with tetrahedrally coordinated tungsten oxide in  $\text{WO}_4^{2-}$  (aq.) and  $\text{Na}_2\text{WO}_4$  (10).  $\text{WO}_4^{2-}$  (aq.) and  $\text{Na}_2\text{WO}_4$  exhibit major vibrational modes at 933 and  $928 \text{ cm}^{-1}$  (symmetric  $\text{W}=\text{O}$  stretch), 830 and  $813 \text{ cm}^{-1}$  (antisymmetric  $\text{W}=\text{O}$  stretch), 324 and  $312 \text{ cm}^{-1}$  ( $\text{W}=\text{O}$  bending vibrations), respectively. Thus, the  $\text{Al}_2(\text{WO}_4)_3$  peak at  $1052 \text{ cm}^{-1}$  is attributed to the  $\text{W}=\text{O}$  stretching mode and the doublet at  $378$ – $394 \text{ cm}^{-1}$  is assigned to the  $\text{W}=\text{O}$  bending mode. The nature of the surface tungsten oxide species in  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalysts is still not resolved. One group postulated the surface species to be bridged-distorted tungstate octahedra (1–3), while two other groups attributed it to a tetrahedral tungsten oxide complex (4–6). The major Raman transition for the 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  occurs around  $970 \text{ cm}^{-1}$ , and has been assigned to the  $\text{W}=\text{O}$  symmetrical stretch (6). The intensities of the major Raman band for  $\text{WO}_3$  ( $808 \text{ cm}^{-1}$ ),  $\text{Al}_2(\text{WO}_4)_3$  ( $1052$

$\text{cm}^{-1}$ ), and 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  ( $970 \text{ cm}^{-1}$ ) were compared after normalization with respect to the laser power applied. The relative Raman intensity ratios for these transitions are 1600 : 40 : 1 per unit power. These Raman intensity ratios were further scaled for the different tungsten oxide contents which yielded the ratios 160 : 5 : 1 per unit  $\text{WO}_3$  content.

The relative Raman intensity ratio of  $\text{WO}_3$  crystallites supported on alumina was also determined as an additional cross-check on the relative Raman intensity ratio estimated from bulk  $\text{WO}_3$ . Both 15 and 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  samples of  $120 \text{ m}^2/\text{g}$  were investigated. The Raman spectrum of the 15%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample, which corresponds to approximately a complete monolayer of the surface tungsten oxide species for this alumina support (6, 7), is shown in Fig. 2a. This sample exhibits the Raman bands of the surface tungsten oxide species on the alumina support and a trace amount of crystalline  $\text{WO}_3$ . The 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample, however, exceeds monolayer coverage

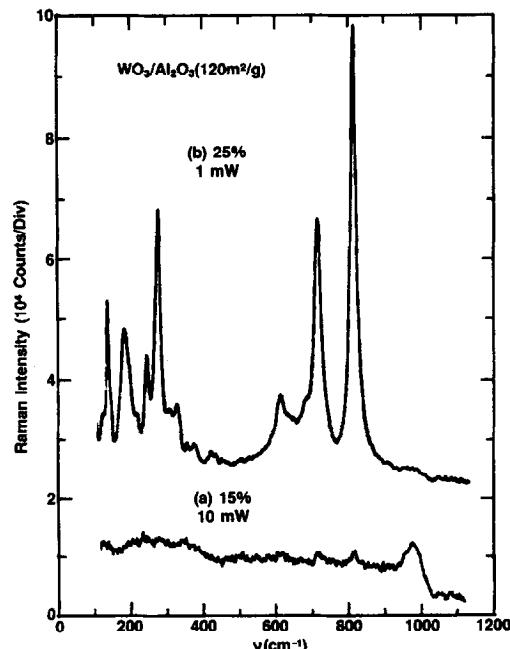


FIG. 2. Raman spectra of (a) 15% and (b) 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  ( $120 \text{ m}^2/\text{g}$ ) obtained with laser power as indicated.

of tungsten oxide on this alumina support and very intense crystalline  $\text{WO}_3$  Raman bands dominate the spectrum (see Fig. 2b). The intensities of the Raman band due to the surface tungsten oxide species are very similar for both  $\text{WO}_3/\text{Al}_2\text{O}_3$  samples as shown in Fig. 3 after scaling for the different applied laser powers over the region  $850\text{--}1150\text{ cm}^{-1}$ . The very similar Raman intensities of this band confirm that both samples possess a complete monolayer of the surface tungsten oxide species. Furthermore, for the 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample the Raman bands of the  $\text{WO}_3$  crystallites dwarf the Raman band of the surface tungsten oxide species. It is reasonable to estimate for the 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample that  $\frac{2}{3}$  of the tungsten oxide is present as the surface tungsten oxide species and that the remaining  $\frac{1}{3}$  of the tungsten oxide is present as crystalline  $\text{WO}_3$  since the Raman intensities of the surface tungsten oxide species are similar for the 15 and 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  samples. From this information the relative Raman intensity ratio per unit tungsten oxide

of the crystalline  $\text{WO}_3$  phase and the surface tungsten oxide phase can be estimated from the data in Fig. 2b. The relative intensity ratio of the major Raman bands for  $\text{WO}_3$  ( $808\text{ cm}^{-1}$ ) and the surface tungsten oxide species ( $970\text{ cm}^{-1}$ ) is determined to be 100 per unit  $\text{WO}_3$  content, and is not significantly different than the ratio of 160 determined from the Raman measurements of bulk  $\text{WO}_3$ . Furthermore, the relative intensity of the major Raman band at  $808\text{ cm}^{-1}$  for the 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample from Fig. 2b and bulk  $\text{WO}_3$  from Fig. 1 is 0.08, and is not significantly different from the expected value of 0.10. The above measurements confirm the extremely strong Raman cross section possessed by the crystalline  $\text{WO}_3$  phase and its apparent *independence* on  $\text{WO}_3$  crystallite size.

From the above data it appears that the light-yellow color of samples containing significant amounts of crystalline  $\text{WO}_3$  as well as the sample volume density does not effect the intensity of the Raman signal from  $\text{WO}_3/\text{Al}_2\text{O}_3$  samples. That this does not appear to be a problem is shown by the 15 and 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  samples of  $120\text{ m}^2/\text{g}$  surface area. The 15% sample was white and the 25% sample was pale yellow. Nevertheless, the Raman bands of the surface tungsten oxide species for both samples have the same intensity as shown in Fig. 3. Also, the intensity of the crystalline  $\text{WO}_3$  band in the 25% sample scaled to that of bulk  $\text{WO}_3$ , with a different density from that of the supported sample, is in good agreement with our cross-section estimates of the two crystalline  $\text{WO}_3$  phases. Thus, the data from Figs. 2 and 3 confirm that our cross-section estimates from Fig. 1 are semiquantitative and useful for estimation of the crystalline and amorphous phases present in supported tungsten oxide systems to within experimental error.

Calcination of the 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample previously discussed at  $1000^\circ\text{C}$  for an additional 16 h yields the Raman spectrum shown in Fig. 4b. The new spectrum is dominated by the Raman bands of crystal-

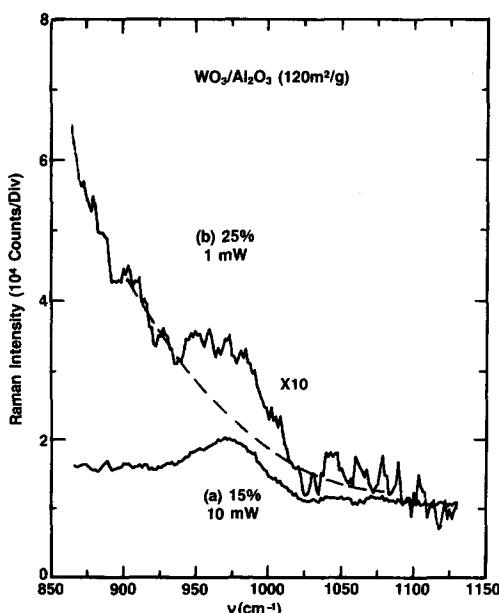


FIG. 3. Comparison of Raman bands of the surface tungsten oxide species for (a) 15% and (b) 25%  $\text{WO}_3/\text{Al}_2\text{O}_3$  ( $120\text{ m}^2/\text{g}$ ).

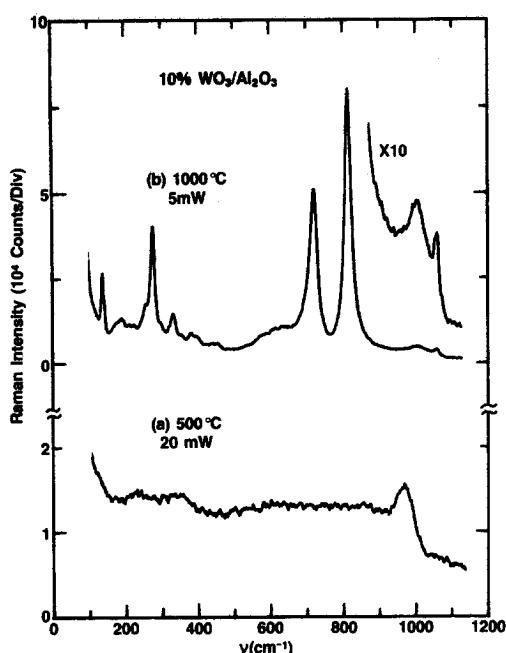


FIG. 4. Comparison of Raman spectra for 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  calcined at (a) 500°C and (b) 1000°C. Note that the amplified plot of (b) from 800 to 1100  $\text{cm}^{-1}$  has the same intensity scale as (a) with the laser power normalized.

line  $\text{WO}_3$ . X-Ray diffraction, however, does not show the presence of the  $\text{WO}_3$  phase and suggests that either the  $\text{WO}_3$  crystals are small ( $<40 \text{ \AA}$ ) or constitute only a small fraction of the total tungsten oxide in the sample. Furthermore, the Raman intensity of the surface tungsten oxide species on the alumina support is about the same for both calcination temperatures. This implies that only a small amount of the surface tungsten oxide species aggregated during the high-temperature calcination to form the crystalline  $\text{WO}_3$  phase. The relative Raman intensity ratio for crystalline  $\text{WO}_3$  and the tungsten oxide surface species can be used to give a first-order quantitative prediction of the crystalline  $\text{WO}_3$  content. For the purposes of this estimate the small amount of  $\text{Al}_2(\text{WO}_4)_3$  present in the 1000°C calcined sample will be ignored. Such a calculation suggests that less than  $\frac{1}{3}$  of the total tungsten oxide content is present as crystalline  $\text{WO}_3$  to yield the Ra-

man spectrum in Fig. 4b, and thereby accounts for the XRD and Raman measurements.

An analogous series of Raman measurements were made on the relative Raman cross section of  $\text{Al}_2(\text{WO}_4)_3$ . The 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample originally calcined at 500°C was calcined at 1050°C for an additional 16 h to quantitatively convert the surface tungsten oxide species to  $\text{Al}_2(\text{WO}_4)_3$  as shown in Fig. 5. The relative intensity of the major Raman bands for  $\text{Al}_2(\text{WO}_4)_3$  (1055  $\text{cm}^{-1}$ ) and the surface tungsten oxide species (970  $\text{cm}^{-1}$ ) is determined to be 4.5 per unit  $\text{WO}_3$  content. This ratio agrees well with the intensity ratio of 5 estimated earlier with bulk  $\text{Al}_2(\text{WO}_4)_3$ . The relative intensity of the major Raman band at 1055  $\text{cm}^{-1}$  for 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  sample calcined at 1050°C in Fig. 5b and bulk  $\text{Al}_2(\text{WO}_4)_3$  from Fig. 1 is 0.10, and is in excellent agreement with the expected value. These measurements confirm the relative Raman cross section of  $\text{Al}_2(\text{WO}_4)_3$  and its apparent *independence* on  $\text{Al}_2(\text{WO}_4)_3$  crystallite size over the range investigated.

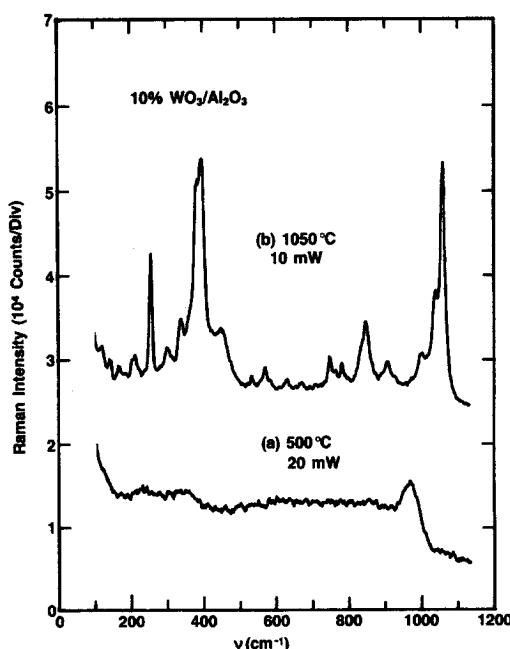


FIG. 5. Comparison of Raman spectra for 10%  $\text{WO}_3/\text{Al}_2\text{O}_3$  calcined at (a) 500°C and (b) 1050°C.

The above measurements demonstrate that the relative Raman cross sections of  $\text{WO}_3$ ,  $\text{Al}_2(\text{WO}_4)_3$ , and the surface tungsten oxide species on the alumina are very different in magnitude and do not change over a wide range of particle size and alumina content. This allows for a first-order quantitative prediction of the different tungsten oxide phases present in  $\text{WO}_3/\text{Al}_2\text{O}_3$ . This information can now be used to examine previous models of the  $\text{WO}_3/\text{Al}_2\text{O}_3$  system.

Salvati *et al.* investigated the  $\text{WO}_3/\text{Al}_2\text{O}_3$  ( $200 \text{ m}^2/\text{g}$ ) oxide system with laser Raman spectroscopy as a function of tungsten oxide loading (6). Below 15%  $\text{WO}_3/\text{Al}_2\text{O}_3$  only the surface tungsten oxide species with bands at 973 and  $333 \text{ cm}^{-1}$  was present on the alumina surface. Above 15%  $\text{WO}_3/\text{Al}_2\text{O}_3$  three additional bands appeared in the Raman spectra at 807, 715, and  $272 \text{ cm}^{-1}$ . These bands were shown to be characteristic of crystalline  $\text{WO}_3$ . X-Ray photoelectron spectroscopy studies demonstrated, however, that the tungsten oxide species present in the catalyst below 30% could not be reduced under conditions where  $\text{WO}_3$  reduction normally occurs. Thus, this species was assigned as an octahedral  $\text{WO}_3$ -like interaction species. The present study shows that because of the very strong Raman cross section of crystalline  $\text{WO}_3$ , only very trace amounts of crystalline  $\text{WO}_3$  in the catalyst, 0.1–0.2 wt% crystalline  $\text{WO}_3$ , are needed to produce the strong Raman peaks observed by Salvati *et al.* Furthermore, the reduction of such a small amount of crystalline  $\text{WO}_3$  cannot be detected with X-ray photoelectron spectroscopy. Therefore, we conclude that aggregates or small crystallites of  $\text{WO}_3$  are present in the 15–30 wt%  $\text{WO}_3/\text{Al}_2\text{O}_3$  samples of Salvati *et al.*, and that the proposal of an octahedral  $\text{WO}_3$ -like interaction species may be incorrect. In support of this statement a 25 wt%  $\text{WO}_3$  on  $\text{Al}_2\text{O}_3$  sample ( $220 \text{ m}^2/\text{g}$ ), which had a Raman band at  $808 \text{ cm}^{-1}$  which was more intense than the band of the surface tungsten oxide species, was shown to have about 1 wt% crystalline  $\text{WO}_3$

present as established by high-resolution X-ray diffraction.

Thomas *et al.* showed that  $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$  catalysts calcined at  $550^\circ\text{C}$ , 7–29 wt%  $\text{WO}_3$ , do not contain aluminum tungstate because of the absence of the characteristic Raman band of  $\text{Al}_2(\text{WO}_4)_3$  at  $1052 \text{ cm}^{-1}$  (2). Even for a coprecipitate of aluminum nitrate and ammonium meta-tungstate sharp Raman signals for  $\text{Al}_2(\text{WO}_4)_3$  were not detected below a calcination temperature of  $1100^\circ\text{C}$ . Only at  $1100^\circ\text{C}$  were sharp  $\text{Al}_2(\text{WO}_4)_3$  Raman bands observed. At lower calcination temperatures,  $550$  and  $900^\circ\text{C}$ , the Raman signals for  $\text{WO}_3$  dominated the Raman spectra. By X-ray diffraction, however, no crystalline  $\text{WO}_3$  was observed and all the samples showed the diffraction patterns of aluminum tungstate. It was proposed that  $\text{WO}_3$  must either be amorphous, microcrystalline, or present in nondetectable amounts. Again, the very strong Raman cross section of  $\text{WO}_3$  relative to  $\text{Al}_2(\text{WO}_4)_3$ , a factor of  $\sim 32$ , accounts for the observation reported by Thomas *et al.* (2).

Thomas *et al.* estimated the Raman cross section of crystalline  $\text{WO}_3$  to the surface tungsten oxide species in  $\text{WO}_3$  on  $\text{SiO}_2$  using aluminum nitrate as an internal standard (11). They determined by this internal standard method that the Raman cross section of crystalline  $\text{WO}_3$  is five to six times higher than that of the surface tungsten oxide species on  $\text{SiO}_2$ . Previous studies have shown that the structure of the surface tungsten oxide on  $\text{SiO}_2$  consists of small 1.2-nm clusters or polymeric units, and that the structure of the surface tungsten oxide on  $\text{Al}_2\text{O}_3$  is more highly dispersed (7). In view of the above it is not unexpected that differences would be observed in the Raman cross sections of the surface tungsten oxides on these two quite different supports. More work is required to understand the origin of the different relative Raman cross sections of surface metal oxide species.

In conclusion, the model of  $\text{WO}_3$  on

$\text{Al}_2\text{O}_3$  which emerges is that tungsten oxide is present on the  $\text{Al}_2\text{O}_3$  surface primarily as a surface oxide species strongly bound to the  $\text{Al}_2\text{O}_3$  surface. At tungsten oxide loading levels which approach a monolayer,  $\sim 0.3 \text{ nm}^2/\text{surface}$  tungsten oxide species, small clusters of  $\text{WO}_3$  may be formed which are readily identified by Raman spectroscopy. The detectable limit of  $\text{WO}_3$  clusters for  $\text{WO}_3$  on  $\text{Al}_2\text{O}_3$  is less than 0.1 wt% content. Aluminum tungstate formation for  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported tungsten oxide catalysts is only observed at extremely high calcination temperatures (at  $1000^\circ\text{C}$  and above) (2, 5). The detectable limit of  $\text{Al}_2(\text{WO}_4)_3$  on  $\text{Al}_2\text{O}_3$  support is less than 1 wt% content.

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#### REFERENCES

1. Thomas, R., Moulijn, J. A., and Kerkhof, F. P. J. M., *Recl. Trav. Chim. Pays-Bas* **96**, M134 (1977).
2. Thomas, R., Kerkhof, F. P. J. M., Moulijn, J. A., Medema, J., and DeBeer, V. H.-J., *J. Catal.* **61**, 559 (1980).
3. Thomas, R., DeBeer, R. H. J., and Moulijn, J. A., *Bull. Soc. Chem. Belg.* **90**, 1349 (1981).
4. Iannibello, A., Villa, P. J., and Marengo, S., *Gazz. Chim. Ital.* **109**, 521 (1979).
5. Tittarelli, P., Iannibello, A., and Villa, P. L., *J. Solid State Chem.* **37**, 95 (1981).
6. Salvati, L., Makovsky, L. E., Stencil, J. M., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **85**, 3700 (1981).
7. Murrell, L. L., Grenoble, D. C., Baker, R. T. K., Prestridge, E. B., Fung, S. C., Chianelli, R. R., and Cramer, S. P., *J. Catal.* **79**, 203 (1983).
8. Chan, S. S., Wachs, I. E., Murrell, L. L., and Dispenziere, N. C., Jr., *J. Catal.* in press.
9. Anderson, A., *Spectrosc. Lett.* **9**, 809 (1976).
10. Busey, R. H., and Keller, D. L., Jr., *J. Chem. Phys.* **41**, 215 (1964).
11. Thomas, R., Mittelmeijer-Hazeleger, M. C., Kerkhof, F. P. J. M., Moulijn, J. A., Medema, J., and de Beer, V. H. J., in "Proceedings, Third International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, Mich., 1979."

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