Characterization of the WO₃/Al₂O₃ System with Low Energy Ion Scattering Spectroscopy

The influence of calcination temperature upon the solid state chemistry of tungsten oxide supported on Al_2O_3 was elucidated with laser Raman spectroscopy (1–4). Laser Raman spectroscopy revealed the amorphous and crystalline structural transformations occurring in the tungsten oxide on Al_2O_3 system. Below monolayer coverage of tungsten oxide on alumina, the supported tungsten oxide phase is present as a highly dispersed surface oxide complex coordinated to the alumina surface (1–11). A close-packed monolayer of the tungsten oxide surface complex on alumina is formed as the surface area of the alumina support decreases at high calcination temperatures, and the minimum possible distance between tungsten centers is achieved (1–3). Additional calcination of the close-packed tungsten oxide monolayer on alumina at still higher temperatures results in further loss in surface area of the alumina support. Simultaneously a portion of the surface tungsten oxide is jettisoned from the monolayer to form crystalline WO_3 which resides on top of the tungsten oxide monolayer. At these high temperatures the alumina support reacts with the WO_3 particles to form $Al_2(WO_4)_3$ by migration of alumina into the WO_3 particles. Further heating of the tungsten oxide on Al_2O_3 results in the conversion of all the tungsten oxide phases to $Al_2(WO_4)_3$, the most stable tungsten oxide compound for the W–Al–O system.

In the present investigation, the effect of calcination temperature upon the tungsten oxide on Al_2O_3 system was examined with low energy ion scattering spectroscopy (LEISS or ISS) because of this technique's unique surface sensitivity to the outermost layers of a sample. Of particular interest were calcination temperatures of 950–1050°C where the γ-alumina support undergoes phase transitions and experiences dramatic decreases in surface area. The effect of these changes upon the surface morphology of the tungsten oxide on Al_2O_3 system is examined with low energy ion scattering spectroscopy in this paper.

The 10% tungsten oxide on γ-Al_2O_3 (Engelhard, reforming grade, ~180 m²/g) catalyst was prepared by the incipient wetness impregnation method by adding an aqueous solution of ammonium meta-tungstate to the alumina powder. The catalyst was subsequently dried at 110°C and calcined in air at 500°C for 16 h. The catalyst was further calcined at 950, 1000, and 1050°C for 16 h to examine the influence of loss in surface area of the γ-alumina support upon the surface morphology of the tungsten oxide–alumina system.

Low energy ion scattering experiments were done on a Leybold Heraeus spectrometer which uses a hemispherical analyzer with a lens. The ion gun was continuously controllable from about 200 to 5000 eV with ion currents at the sample ranging from about 1 nA/cm² to several μA/cm². $^4He^+$ ions were used as the primary source, and the laboratory scattering angle for ion scattering is 120°.

The W/Al ratios obtained with low energy ion scattering for 10% tungsten oxide on alumina calcined at 950, 1000, and 1050°C are shown in Fig. 1. The data was collected with 500 eV $^4He^+$ to maximize first layer contributions. Note the dramatic *increase* of the W/Al ratio upon increasing the calcination temperature from 950 to 1000°C, and the dramatic *decrease* of the W/Al ratio upon further increase of the cal-
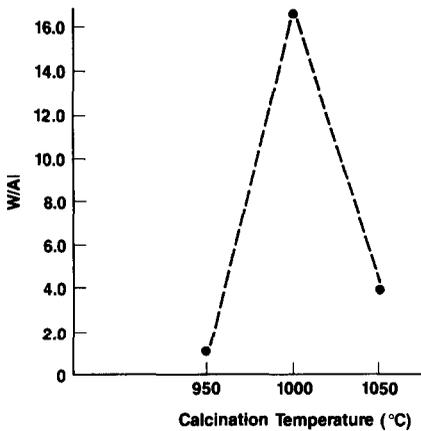
FIG. 1. Ion intensity ratios for 10% WO_3/Al_2O_3 as a function of calcination temperature.

cination temperature from 1000 to 1050°C. The increase in the W/Al ratio occurred at the same temperature that laser Raman showed WO_3 crystallites to be formed (1–3). The LEISS data shows that, as suggested by the Raman data, the WO_3 crystallites are forming on top of the tungsten oxide–alumina surface and effectively shield the underlying Al_2O_3 support from the $^4He^+$ ions. The unusually large increase in the LEISS W/Al ratio is probably enhanced by the migration of some of the WO_3 crystallites to the exterior of the alumina particles (the region sampled by LEISS). Further increase in the calcination temperature from 1000 to 1050°C, which results in the formation of $Al_2(WO_4)_3$ (1–4), causes a dramatic decrease in the LEISS W/Al ratio. This result is consistent with the earlier conclusion that at these temperatures the alumina is migrating toward the surface and is corrosively reacting with the WO_3 particles.

Further evidence of such tungsten oxide and alumina movement can be found by examining the ion survival probability of $^4He^+$. At constant scattering angle this quantity can be defined as follows (assuming only Auger transitions) (12):

$$ISP = A[\exp(-b/V)]$$

where A contains experimental constants

and shadowing terms, V is the perpendicular velocity of the scattered ions, and b is a characteristic neutralization constant. The term b does include a small contribution from the incident energy of the ion beam, but under the range of energies normally used in LEISS, ~500–2000 eV, the contribution is insignificant (12). Ions arising from different depths should have different slopes or intercepts when the reciprocal of the perpendicular velocity is plotted versus the log of ion survival probability. The slope of the resulting line corresponds to the neutralization constant, b, that is sensitive to the electronic structure and the depth distribution of the scattering centers. However, in general, the actual value of the ISP is more sensitive to where the scattering center lies relative to the surface. The higher the ion survival probability of an element at a given velocity, the higher is the likelihood that the scattering center is on the surface of the sample.

The log of the ion survival probability versus the reciprocal of the velocity is plotted in Fig. 2 for 10% tungsten oxide on alumina calcined at 950 and 1050°C. For the 950°C calcined sample, which contains a close-packed monolayer of surface tungsten oxide on alumina (1–3), the ion survival probability from tungsten is greater than from aluminum suggesting that tung-
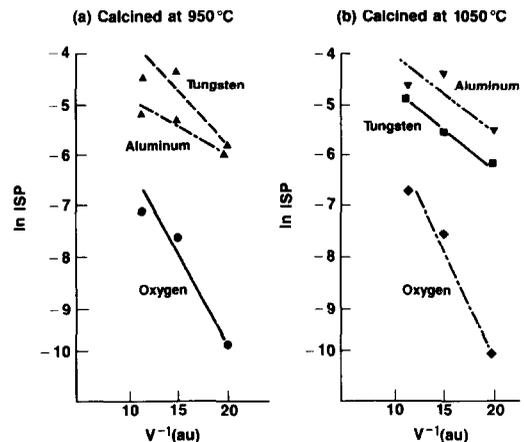
FIG. 2. Ion survival probability for 10% WO_3/Al_2O_3.

sten is residing on top of the alumina support. For the 1050°C calcined sample, which contains crystalline $Al_2(WO_4)_3$ (*1–3*), the ion survival probability from aluminum is greater than from tungsten suggesting that tungsten oxide is *not* residing on top of the alumina support and is consistent with the incorporation of tungsten into the bulk $Al_2(WO_4)_3$ structure. Only the neutralization aspect of the change in scattering intensity is treated here and it would be wrong to imply that other factors, such as shadowing and the target atom's electron configuration, do not play a role. However, their effects do not alter our conclusions.

The low energy ion scattering studies of tungsten oxide on alumina calcined at 950, 1000, 1050°C provide us with additional information about the surface morphology of the tungsten oxide-on-alumina system. The tungsten in the close-packed tungsten oxide monolayer resides *on* the alumina support. The WO_3 crystallites that result from the desurfacing of the alumina support reside *on* top of the close-packed tungsten oxide monolayer. The $Al_2(WO_4)_3$ crystallites that are formed from the reaction of alumina and the WO_3 crystallites possess a lower surface concentration of tungsten oxide because of the incorporation of tungsten into the bulk $Al_2(WO_4)_3$ structure. The present LEISS results complement and confirm the solid state chemistry of tungsten oxide on Al_2O_3 earlier elucidated with laser Raman spectroscopy (*1–4*). Furthermore, the surface sensitive LEISS data demonstrates that the laser Raman technique, nominally a bulk spectroscopy, was indeed monitoring the changes occurring at the surface of the tungsten oxide-on-alumina system.

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